THE JOURNAL
OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

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CONTENTS

The Application of Colorants to Leather

The Chemical and Physical Nature of Leather Fibers in Relation to Dyeing *By* R. STUBBINGS - - - - 514

Coloring of Leathers on Which Penetration is Desired *By* J. A. CASNOCHA - - - - - - - - - - - 520

The Spray or Brush Dyeing of Leather *By* C. H. GEISTER - 523

Dyes and Dyeing Processes for Special Properties of Color *By* J. S. KIRK - - - - - - - - - - - 526

Instrument for Measuring Thermal and Elastic Behavior of Hide and Modified Hide Materials *By* J. G. FEE, R. R. CALHOUN, and L. P. WITNAUER - - - - - 530

Zirconium Tannage. VII - Direct Utilization of Insoluble Zirconium Derivatives *By* I. C. SOMERVILLE and W. J. RAU - 542

Discussion of Adhesion Test for Leather Finishes - - 556

Life Lines - - - - - - - - - - - 558

ALCA News - - - - - - - - - - - 560

Abstracts - - - - - - - - - - - 564

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IMPORT - EXPORT

SERVICE...
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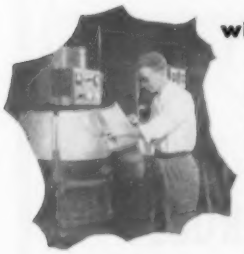
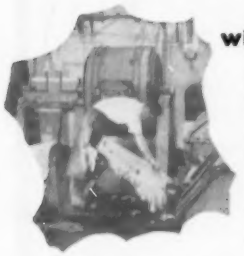
...backed by Rohm & Haas Research



with modern Leather Laboratories

Our technically trained leather chemicals salesmen working in the field have the complete backing of a highly specialized leather research staff working in the Rohm & Haas Leather Laboratories. For years, these specialists in leather chemistry have been engaged in a study of leather, its uses and its many process problems. The knowledge and experience gained over the years from this research are available to you through your Rohm & Haas salesman.



with a practical Miniature Tannery

Process problems that cannot be handled in the field are brought to our experimental tannery for detailed study and analysis. Here we have simulated a commercial leather-making operation, a tannery-in-miniature which provides small-scale facilities for running tests on many kinds of leather. Problems are handled in a thorough, practical way.

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Continuous research in the Rohm & Haas leather chemicals laboratories has resulted in the development of new and improved leather chemicals for the tanner.

Rohm & Haas leather chemicals are world famous...

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TAMOL—the dye assist that made pastel colors practical.

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PRIMAL—leather finishing materials in the form of aqueous dispersions of acrylic resins.

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TYPICAL A.L.C.A. ANALYSIS

	Ordinary	Clarified
TANNIN	61.55	64.34
NON-TANNIN . . .	16.03	17.14
INSOLUBLES . . .	1.70	0.72
WATER	20.72	17.80

As a retanning agent for chrome tanned leather, Myrtan possesses many advantages, such as smooth and strong grain, good color and break, as well as a round feel.

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2 to 1

That's the standing of LEATHER AND SHOES in the tanning industry

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But *readership* is even more important. A recent study revealed that at least 3500 top level executives in the tanning industry are reading LEATHER AND SHOES.

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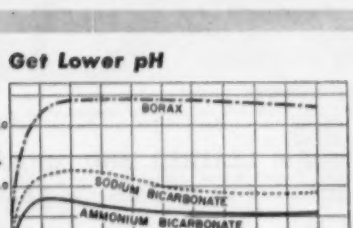

Pounds of hydrochloric acid neutralized by 1 lb. of alkali

Get Lower pH

Comparative pH of solutions at various concentrations

Get All These Advantages!

- ★ Better finish and uniform quality.
- ★ Upgrading leathers.
- ★ More uniform dyeing.
- ★ Deeper penetration.
- ★ Improved grain.
- ★ Low pH — a 1% solution has a pH of only 7.8

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ARKOTAN B is a syntan that assists in the production of a smoother grain, improved tensile strength, fuller and rounder feel and a clear, even color.

ARKOTAN B assists in the solubility of your extracts, permitting greater penetration and better take-up and reduces the sludge in the bath when solid Quebracho is used.

ARKOTAN B when used in the color pit, wheel or tail liquors improves the appearance of the grain and maintains the correct acidity in the tail liquor without the addition of acid at this point.

ARKOTAN B is used extensively in the re-tan wheels to produce added weight. Excellent for use on chrome re-tan upper leather where a tight break and solid feel is required.

Samples or demonstration of **ARKOTAN B** are available upon request.

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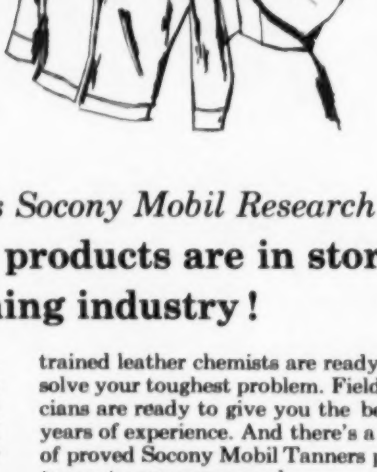
MOBIL TANNERS NEWS

- *Announcing Mobiltan 275—newly developed fat-liquoring agent for pasted-side upper leather.*
- *Research and Development Report on new and improved products in store for tanners.*
- *Catalogue of Socony Mobil Tanners Products, including new nomenclature.*

1957 Edition

Improved waterproofing compounds for upper leathers are being developed and tested by Socony Mobil scientists. The goal is upper leathers with a new degree of water resistance.

Tanners products to make suedes water-repellent and dry-cleanable—long an aim of the leather industry—are now in the development stage at Socony Mobil's leather products laboratory.



Thanks to Continuous Socony Mobil Research

New and improved products are in store for the tanning industry!

Socony Mobil leather chemists are constantly at work *for you!* Two of their most significant projects are shown above. Water-repellent, dry-cleanable suedes and improved water-proofing compounds for upper leathers.

This constant search for new methods and new products is just one of the many ways Socony Mobil serves the leather industry. Extensive laboratory facilities and trained leather chemists are ready to help solve your toughest problem. Field technicians are ready to give you the benefit of years of experience. And there's a full line of proved Socony Mobil Tanners products to meet your every need.

* * *

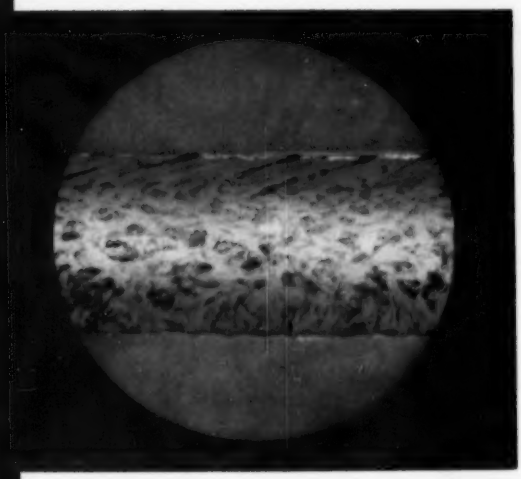
You can rely on Socony Mobil Research—to speed progress . . . increase profits for the tanning industry!

Socony Mobil Tanners Products

SOCONY MOBIL ANNOUNCES

Mobiltan 275

Specifically developed for fat-liquoring of pasted-side upper leather!



Cross-section photomicrograph illustrates controlled penetration of Mobiltan 275. Special qualities permit surface nourishment and enough penetration to give the desired mellowness.

Mobiltan 275 is a carefully compounded, relatively complete fat-liquor that will give excellent results in both full and corrected grains of pasted-side upper leather. Years of research and exhaustive field testing have resulted in a compound with these desirable properties:

- Non-oxidizing and light fast
- Controlled penetration for balanced lubrication
- Forms a stable emulsion at normal operating temperatures
- Exhausts readily with normal running time
- Compatible with resin re-tannages
- Low moisture content

For more information on how Mobiltan 275 can improve your production and cut your operating costs, contact your Socony Mobil representative.

Mobiltan 275 in solution shows an alkaline pH reading — truly an alkaline fat-liquor.

Mobil

First choice with Tanners since 1866

SOCONY MOBIL

Tanners products

Check list for available products and name changes

FORMER BRAND NAME	NEW BRAND NAME
Mobil Solene A	Mobilon A
Mobil Solene B	Mobilon B
Mobil Solene No. 5	Mobilon C
Mobil Sole Waterproofing Compound No. 1	Mobilon D
Mobil Sponging Compound No. 2	Mobilon 2
PD 458-B	Mobilon 3
Mobil Setine No. 2	Mobilset 2
Mobil Setine No. 3	Mobilset 3
Mobil Curriers Oil No. 3	Mobilset A
Mobil Curriers Oil No. 4	Mobilset B
Mobil Curriers Vacgrease A	Mobilkor A
Mobil Curriers Vacgrease D	Mobilkor D
Mobil Curriers Polishing Compound	Mobilkor P
Mobil Curriers Vacgrease W	Mobilkor W
Mobil Curriers Hard Grease No. 6	Mobilkor 6
Mobil Curriers Hard Grease No. 13	Mobilkor 13
Mobil Vacrome	Mobilcrome 1
Mobil Nappellent AA	Mobilnap AA
Mobil Sulfoline A	Mobiltan A
Mobil Sulfoline G	Mobiltan G
Mobil Sulfoline O	Mobiltan O
Mobil Sulfoline S	Mobiltan S
Mobil Sulfoline U	Mobiltan U
Mobil Sulfoline W	Mobiltan W
PD 872-A	Mobiltan X
Mobil Sulfoline 100	Mobiltan 100
PD 275-D	Mobiltan 275
Mobil Sulphonated Setine No. 3	Mobiltan 300
Leather Oil No. 7	Tanrex 7
Leather Oil No. 8	Tanrex 8
Leather Oil No. 15	Tanrex 15
Leather Oil No. 16	Tanrex 16

Socony Mobil Oil Company, Tanners Division
150 East 42nd Street
New York, New York

I am interested in further information on Socony Mobil Tanners Products. Please have a Socony Mobil Tanners Representative call on me.

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Mobil

SOCONY MOBIL

Tanners Products

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WHITE BOTTOMS —
for clean pastel shades!

VARIED GRAIN EFFECTS —
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Get better leather

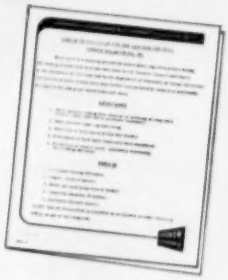
2 to 3 days faster

Reports from tanners and work in our own laboratory continue to point up these advantages of Hooker sodium tetrasulfide for soaking:

1. **Faster soaking.** Dry skins soaked with 0.7% of sodium tetrasulfide at 65° to 70° F. are ready for drumming in only 24 hours. Some tanners report cutting soak for flint dried steer hides from four or five days to 48 hours—saving two or three days.

2. **Higher yield, better quality.** Sodium tetrasulfide produces more uniform soaking through removal of cement substance, more uniform unhairing and liming. It reduces or eliminates fine hair trouble and hard spots (especially hard shoulders). Result: higher yield of better quality leather.

3. **Lower cost.** Hides move through process faster. Shorter soaking offers less possibility of damage, better yield. All result in more efficient, economical tannery operation.



Bulletin gives complete story.

To help judge how sodium tetrasulfide can fit into your operations, send for our Bulletin 505. It describes fully the uses and advantages of sodium tetrasulfide, recommended soaking procedures for various skins and hides.

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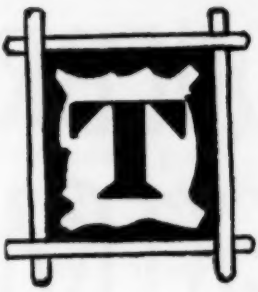

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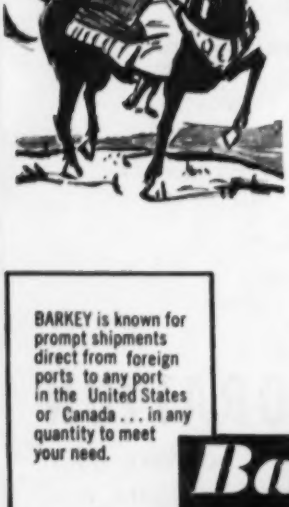

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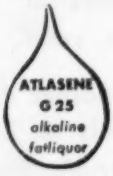
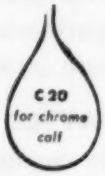
Every industry has its famous names. In tanning, Atlas, and the products it has developed through the years, all are "household names"—respected because they represent the finest of their kind and for their purposes.

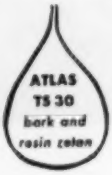


How many of those names do you recognize as "old friends?" How many of the new ones are you familiar with?



Atlas, keeping apace of, and frequently leading the way to, new progress in tanning, brings you the products best suited to your needs.

It is a fact that when tanners change to Atlas Fatliquors, few ever change again.



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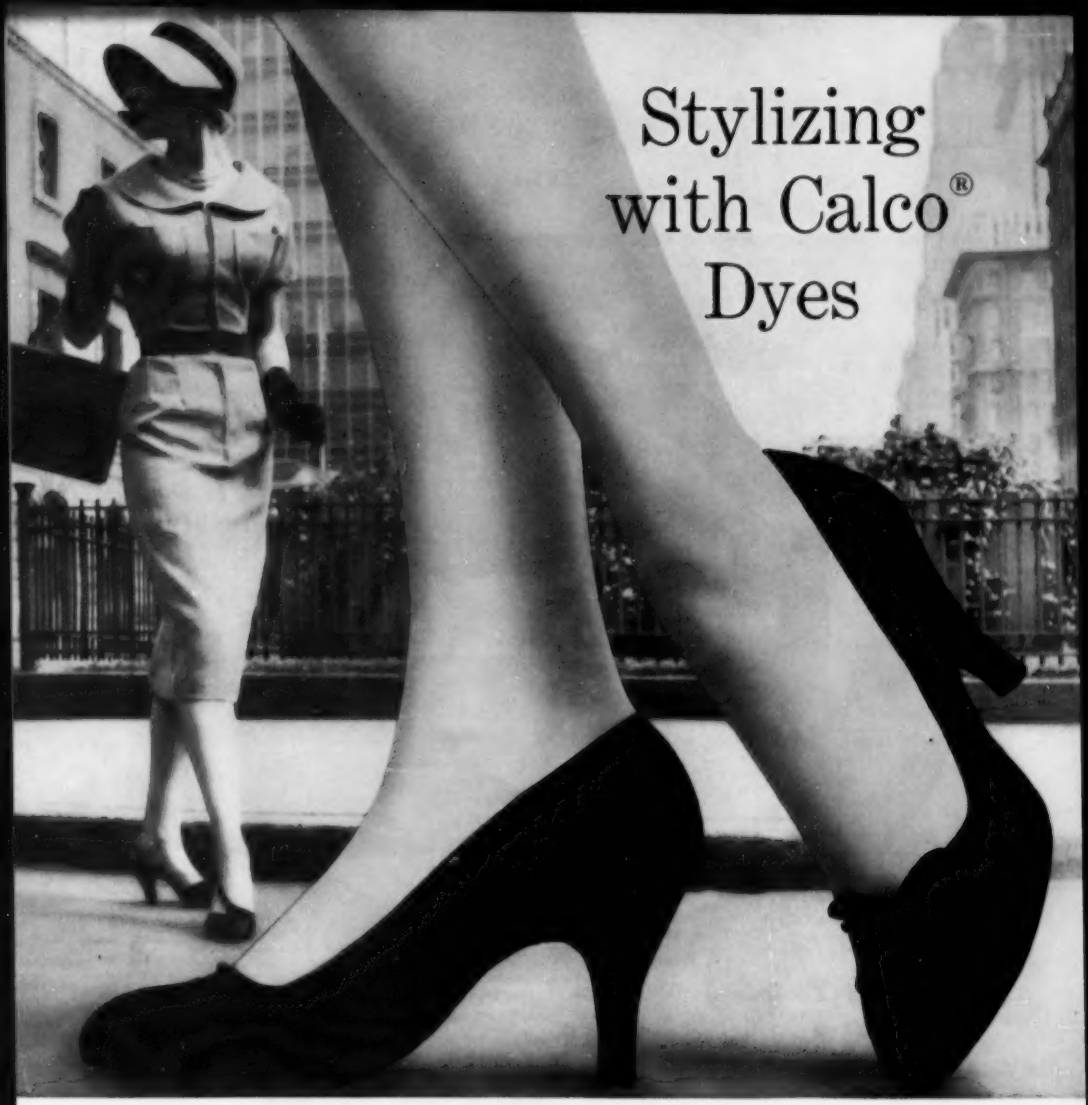

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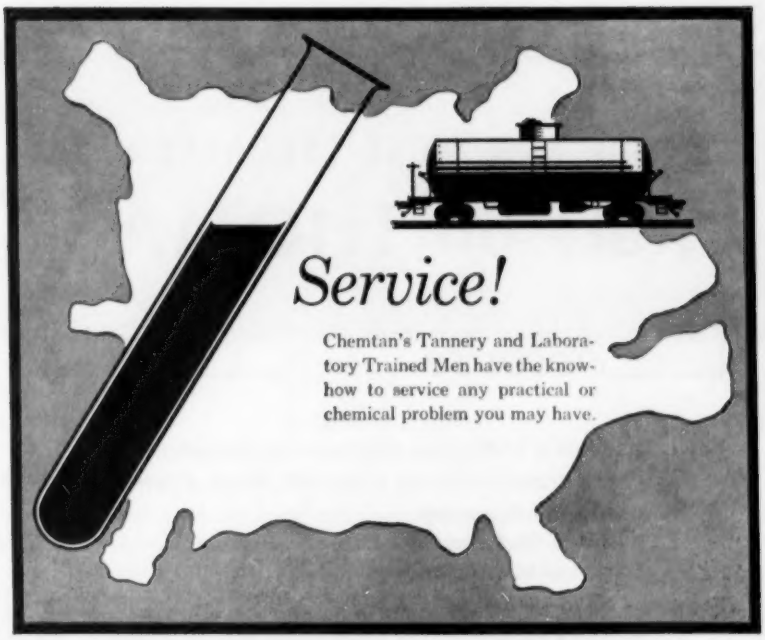
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The Application of Colorants to Leather

Four Papers presented during the Perkin Centennial

New York, September 10–15, 1956

The 100th anniversary of the discovery of the first coal tar dye by Sir William Perkin was fittingly observed by the holding of a week-long symposium on all phases of the chemistry and application of dyes. The program was planned and conducted by the American Association of Textile Chemists and Colorists with the cooperation of 27 scientific, technical, and trade organizations. As one of these participating bodies, the American Leather Chemists Association sponsored a discussion of "The Application of Colorants to Leather" on September 11, 1956. The following four papers were presented on that occasion and are published by permission of the Centennial Committee and the A.A.T.C.C.

THE CHEMICAL AND PHYSICAL NATURE OF LEATHER FIBERS IN RELATION TO DYEING

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Leather consists of a three-dimensional anisotropic network of tanned collagen fibers. The top surface (or grain) consists of very tightly woven fine fibers interspersed with deep pore pockets, whereas the main portion of the leather consists of much coarser fibers arrayed in three dimensions and containing no pores. Both the chemical nature of the individual fibers and the physical nature of the fiber mat affect the dyeing properties.

EFFECT OF THE CHEMICAL NATURE OF THE FIBERS ON DYEING

Untanned Fibers.—The untanned collagen fibers consist of long polypeptide chains with many polar side chains. It is these polar side chains that differentiate collagen from silk and cause it to be similar to wool, as shown in Table I.

These polar side chains represent the sites at which dyes are bound to the fibers, and their availability from chemical, stereochemical, and physical viewpoints determines the dye-binding capacity of the fibers. Probably the most important single chemical property in connection with the dyeing of these polar side chains is their charge. Generally speaking, the polar side chains are fully charged at the isoelectric point of the protein (that is, the carboxylic groups have a negative charge and the basic nitrogen groups have a positive charge.) As the pH is altered or various groups are chemically

TABLE I

SIDE-CHAIN GROUPS EXTENDING FROM POLYPEPTIDE BACKBONE IN VARIOUS PROTEINS

Side-chain weight as per cent of total protein weight

Side-Chain Groups	Silk	Collagen	Wool
Non-polar groups (–H, $-CH_3$, $-SCH_3$, etc.)	6.3	14.1	12.0
Hydroxy groups (serine, hydroxy proline, etc.)	12.5	7.4	8.8
Sulfhydryl groups (Cysteine)	0.0	0.0	4.9
Basic groups (amino, guanidino, imidazole)	0.6	8.0	8.0
Acidic groups (Carboxyl)	Not reported	8.4	10.8
Total polar groups	13.1	23.8	32.5
Total non-polar groups	6.3	14.1	12.0
Total side groups	19.4	37.9	44.5

masked, a discharging of either the acidic or the basic groups takes place. This changes the reactivity of the polar side chains for various types of dyes. For example, a simple acid dyestuff will combine with collagen fibers at low pH values but not at all at high pH values, as is shown for Orange G in Figure 1. The Orange G combines with the basic groups of the fiber, but as these groups are discharged at higher pH values, less and less dye combines.

Tanned Fibers

1. *Chrome tanned.*—Most leather is tanned by means of complex basic chromic salts and the tanning reaction is primarily a combination and cross-linking through the carboxylic groups of the protein side chains. The reaction is limited to a pH range of about 2–4 since below this pH range the carboxyl groups are discharged and chrome does not bind, and above this range the basic chrome salt precipitates. The chrome-tanned fiber presents an entirely different chemical surface to dyes from the untanned fiber. The chromium complex forms associated linear polymers which have high complexing ability for organic anions such as dyestuffs. In fact, fibers tanned to a chrome content common to commercial leather have an affinity for

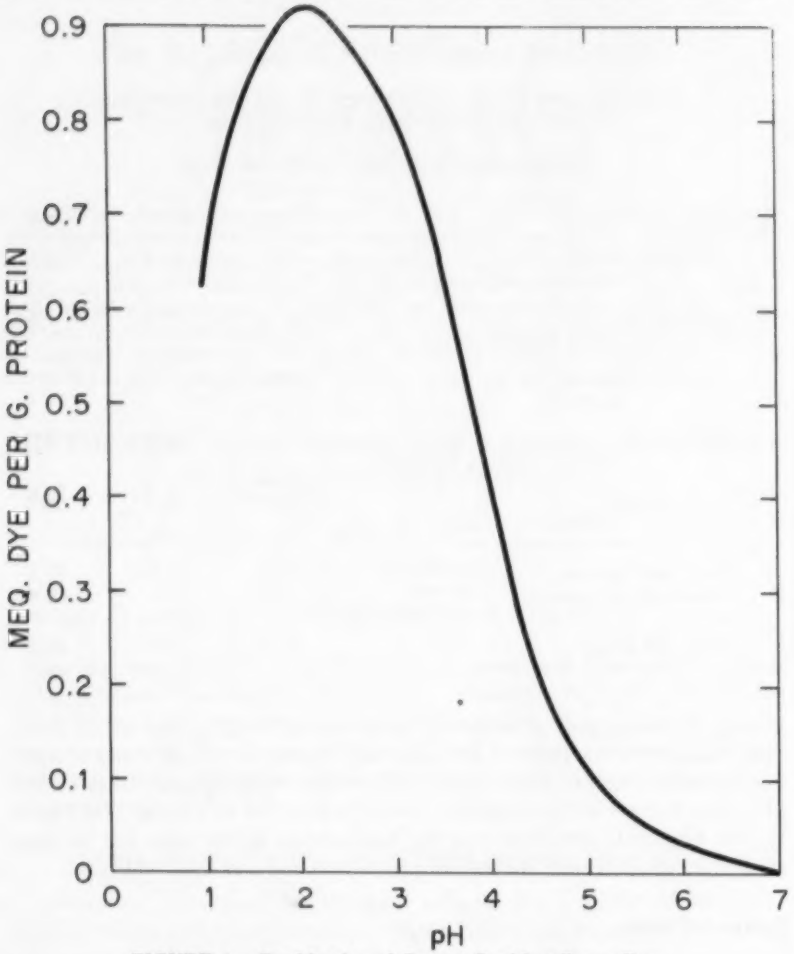

FIGURE 1.—Combination of Orange G with collagen fiber.

acid dyes of 2 to 3 times that of untanned fibers as shown in Figure 2 for Orange G. The pH of the chrome-tanned fibers at the time of dyeing has an additional effect on the dye takeup and this varies with the type of dyestuff used as shown in Figure 3. This pH effect is complicated, but, in general, acid dyes tend to have maximum affinity at low pH levels, while direct dyes have maximum affinity at higher pH levels.

2. *Chemical modification of chrome-tanned fibers.*—If non-colored anionic materials are reacted with the chrome-tanned fibers prior to dyeing, the dye

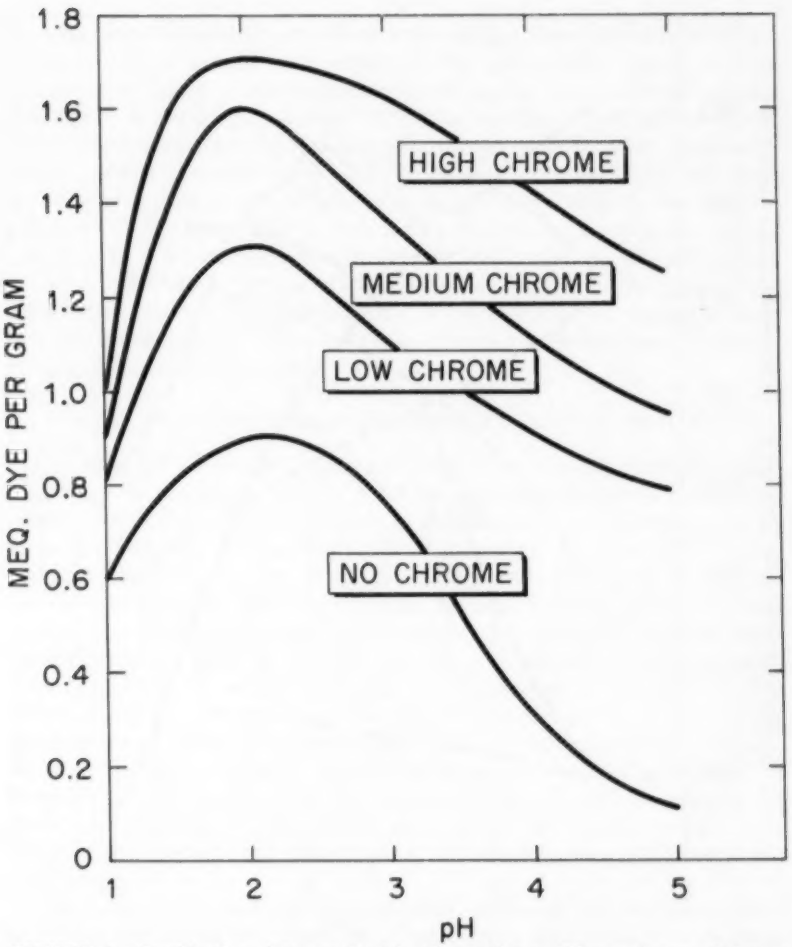

FIGURE 2.—Combination of Orange G with collagen fiber at different degrees of chrome tannage.

affinity is usually affected. For example, the addition of an organic acid which forms stable complexes with the chromium usually reduces the affinity for a dyestuff. In practical leather dyeing, this effect is used to get better leveling and penetration of a dye on the leather. Normally for this purpose anions of relatively high molecular weight (syntans) are employed. Adding cationic materials of high molecular weight to chrome-tanned leather has the opposite effect and usually results in deeper-colored surface dyeing.

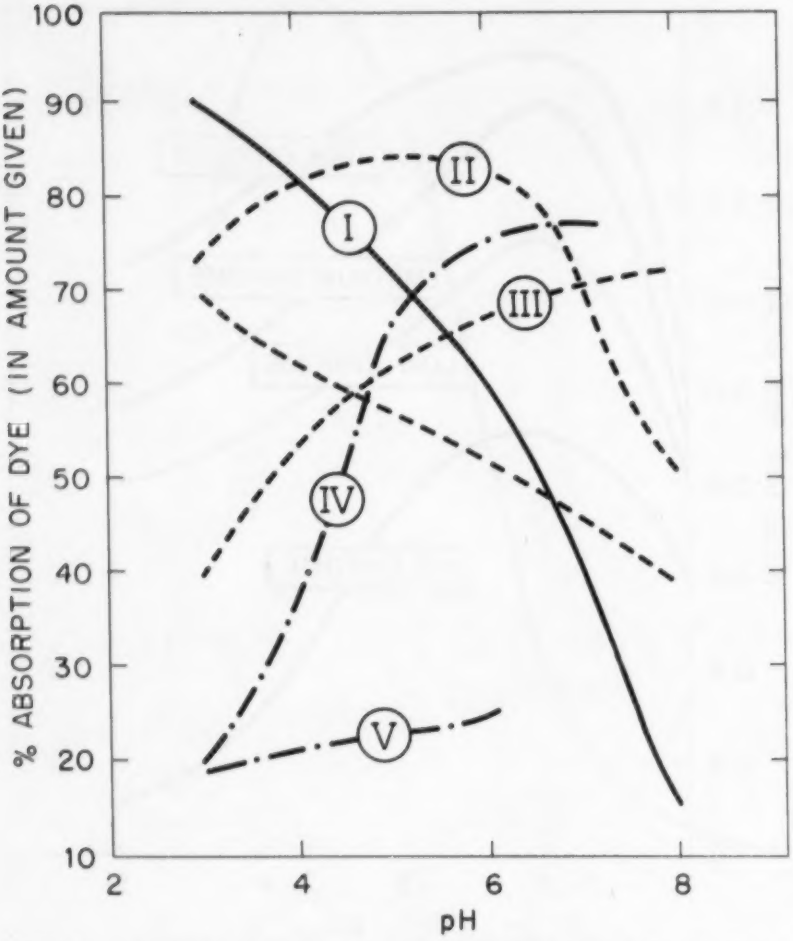

FIGURE 3.—Takeup of various dyes by chrome-tanned hide powder at equilibrium with excess dye present. Curve I–Orange G, Pontacyl Carmine B, and Pontachrome Flavine A; Curve II– Pluto Orange GRL, Fastusol Turquoise LGA, and Calcomine Dark Green BG; Curve III–Erie Black GX00, and Direct Fast Brown TSN; Curve IV–Chrysoidine GN; Curve V–Rhodamine B.

_____Acid _ _ _ _Direct _ . _ . _ . _ . _Basic

3. *Vegetable-tanned fibers.*—Vegetable-tanned fibers act very differently from chrome-tanned fibers in their reactions with dyestuffs. The vegetable tannins usually used are complex mixtures of polyphenols of varying molecu-

lar weight which probably combine with the collagen fibers primarily hydrogen bonds to peptide groups, and secondarily by electrovalent bonds to basic nitrogen side chains. Commercial vegetable leather contains much greater amounts of tanning agent (about 50%) than chrome-tanned leather (about 5%). The combination of the vegetable tannin with the fiber produces a greatly altered chemical surface to the dyestuff. Vegetable-tanned fibers can be dyed readily by all the basic dyes but also react with some of the acid and direct dyes. The pH of the fiber prior to dyeing has a great effect on the dye affinity. The reduction of acid dye affinity by the presence of vegetable tannin is used in the dyeing of chrome-tanned leather for leveling of the color. This process, called mordanting, is employed in the dyeing of most chrome-tanned leather. The mordanting process also makes possible the use of basic dyes on chrome-tanned leather.

EFFECT OF THE PHYSICAL NATURE OF THE LEATHER ON DYEING

The dyeing of leather is complicated by the fact that the top and bottom surfaces of the leather have entirely different physical structures which allow penetration and reaction of dyestuffs in different ways. The top surface or grain has deep pore pockets which extend to a depth of about 0.020 inches and into which the dye can flow fairly readily when the leather is flexed in the drum. The grain fibers that occupy the area between the pore pockets are very fine fibrils in the plane of the surface. Some dyestuffs seem to enter these grain fibers from the sides of the pore pockets, while others penetrate downward from the surface of the grain. The reason for this different behavior is not at present understood, but it is undoubtedly related to the physical nature of the grain surface and probably to the molecular size and shape of the dye molecule. This variation in the mode of penetration of dyestuffs into the leather grain surface makes estimates of the penetrating power of a given dye very difficult, since almost all dyes penetrate to the depth of the hair root but do not spread out through the grain layer to the same degree.

This difficulty, coupled with the changes in combining capacity of individual dyes with pH, makes the prediction of penetrating power based on chemical structure almost impossible. In present practice the problems of penetration and surface color (especially for dye mixtures) have to be solved by patient trial and error experimentation. In this regard the experience of both the dyestuff manufacturer and the tannery colorist are of much greater value than any presently available physical or chemical data concerning the dyes themselves.

In the U. S. the acceptance of the new dyes was at first very conservative. Unofficial reports indicate that in 1866 at Boston there were imported 1000 lb. of coal tar dyes, which were disposed of in about 6 months.—August Merz, *Encyclopedia of Chemical Technology*.

COLORING OF LEATHERS ON WHICH PENETRATION IS DESIRED

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In leather coloring we encounter numerous difficulties which ordinarily do not burden dyers of other materials. First of all, we concern ourselves with a substrate that lacks uniformity and over which we have only limited control. Those of us who deal with leather are well aware of the differences that exist from skin to skin, and we also recognize the variations present within the same skin. The heterogeneous nature of the stock is fully reflected in its coloring properties, but the affinity of dyes, and consequently the levelness of the shades, depends not only on the chemical and physical structure of the protein fibers but also on the character and the distribution of the tanning agents, fatliquors, and other reagents that precede or follow coloring.

In addition to surface appearance, many types of leather require complete penetration of the dye. Thus to the leather colorist the third dimension is of much greater significance than it is to the textile dyer. Cross-coloring is essential on suedes, whether they are used for shoes or handbags; on sheep suede and grains for garment leather; on glazed kid for shoe leather; and, to a certain extent, on side leather. Uniform penetration of the dyes is of particular importance on suedes which are buffed after coloring, since on this type of leather it is the layer of fibers that is exposed by removing the surface that actually becomes the criterion of levelness and shade. Satisfactory results are obtained only by uniform tanning, by careful selection of dyes, and by their proper application.

The most popular colorants for these leathers are the ordinary water-soluble synthetic dyestuffs, anionic or cationic, but particularly the former. Essentially there are two ways in which the required penetration is obtained; however, the procedure that is employed depends on the type of leather and the desired shade—or better, the depth of shade. The available methods are: (1) selection of dyes that have good inherent penetration, and (2) alteration of the conditions of application and of the leather so as to reduce its affinity for the dyes. Once the affinity is reduced, it is possible to force through the surface layers of the leather even those dyes that have comparatively low inherent rates of penetration.

Inherent penetration has been subjected to many investigations, but the explanation of this phenomenon is not as simple as it might appear to the casual observer. Ordinarily the anionic dyes that the textile colorists place in the so-called "acid dyeing" group are the ones that exhibit appreciable penetration on leather. Some investigators have associated molecular weight

with penetration; some, the acid character of the dyes; while others have considered ratios of molecular weight to the number of sulfonic groups as bearing responsibility for the phenomenon. Still others have attributed the inherent penetration to the balance and distribution of charged groups on the dye molecules, while the colloid chemists have centered their attention on the size of the particles that make up the dye dispersions. It appears reasonable to assume that all these factors, some of which are interrelated, contribute to the total effect that is known as inherent penetration. However, it can be stated with safety, and without pinpointing the cause, that penetration is inversely proportional to affinity. Dyes such as Xylene Fast Orange G (C. I. 27) and Xylene Cyanole FF (C. I. 715) penetrate more than Rocceline S (C. I. 176), and Resorcine Brown R (C. I. 235), because the latter possess greater affinity for the leather. In Table I appear penetration indices of a few typical anionic dyestuffs that are employed in the leather industry. The indices have been determined under standardized conditions, and they represent the inherent penetration of the particular dye as exhibited on chrome-tanned calf leather. The higher the index number, the greater is the penetration of the particular dye.

TABLE I

INHERENT PENETRATION OF DYES

Dyestuff	Color Index	Penetration Index
Xylene Cyanole FF	715	17
Xylene Fast Orange G	27	15
Crocein Scarlet M00	252	10
Naphthol Blue Black B	246	7
Rocceline S	176	6
Resorcine Brown R	235	5
Chloramine Red 3B	382	4
Chloramine Green 2B	593	3

Since penetration is associated with affinity, the former can be altered by changing the affinity of the leather for the dyes. This can be accomplished by blocking the reactive groups of the leather or by adding other groups that can be utilized by the dyestuffs. More specifically, penetration can be altered by increasing or decreasing the pH of the dye-leather system, by masking the chromium complex that is present in the chrome-tanned leather, or by neutralizing the electrical charges on the leather through treatment with various anionic or cationic auxiliaries. In addition to the aforementioned factors, high concentrations of electrolytes also increase penetration of these anionic dyes that depend largely on primary valences for their combination with leather. In cases where other reactive forces predominate or enter into

the picture, the temperature of application has been observed to play a role. In conjunction with these chemical or physico-chemical methods, we can utilize more or less purely mechanical means, such as subjecting the leather to flexing while exposing it to the dye solution, increasing the concentration of the dye bath, prolonging the time of exposure (provided there is some unfixed dye left in the liquor), or increasing the amount of dye. Many of these factors are interrelated: some may not be used on certain types of leather because they affect the quality of the finished product, while others might prove uneconomical or impractical.

It is the task of the leather colorist to employ and adjust these factors and produce the desired results without resorting to any procedure that will be detrimental to the quality of the leather. For example, if he is to color with anionic dyes a deep brown on kid suede, he will alter the leather and the conditions of application rather than employ very penetrating dyestuffs which are difficult to exhaust when used in heavier concentrations. Ordinarily suedes are colored out of crust; that is, the leather is fatliquored and dried first, and only then is it rewetted and dyed. This process alters the chromium complex and the fibers in such a way that they exhibit a reduced affinity for the colorants. Consequently, the leather is easier to penetrate. As a further aid to cross-coloring, the colorist will employ in the dye bath some mild alkali, such as ammonia, which will have three simultaneous effects:

1. It will neutralize some of the charged amino groups ($[—NH_2]^+$) of the protein.
2. It will basify the chromium complex by displacing water and sulfate groups with hydroxyl groups, which in turn are more difficult to replace by the dye anions.
3. It will retard the formation of larger agglomerates in the dye bath and thus facilitate the penetration of smaller particles.

In order to secure mechanical assistance, the leather will be colored in large rotating drums where it will undergo considerable agitation and flexing, and the bath will represent up to 3% dye concentration, using a total of approximately 20% dyestuff based on the dry weight of the leather.

On the other hand, if we are to color side leather a light pink with good penetration, we will employ a fractional percentage of highly penetrating anionic dyes which will cross-color the freshly tanned leather at a relatively low pH. (The quality of this type of leather suffers at higher pH levels.) In order to reduce the affinity of the chrome-tanned leather, which bears positive charges, it will be treated first with some anionic colorless compounds known as "syntans" (sulfonic acids of phenol-formaldehyde condensates). These will neutralize the electrical charges and occupy the reactive sites of the leather that are ordinarily occupied by the anionic dyes. Thus the treatment will compel the dyes to penetrate the leather in search of available

reactive groups. Even though this type of leather will also be colored in rotating drums, they will revolve slowly, and the dye bath concentration will be considerably lower than that used for suedes.

The remarks made so far pertain mainly to chrome-tanned leather on which anionic dyestuffs are primarily employed, but the same principles hold true for vegetable and other tannages. Vegetable tannage creates low affinity for many of the anionic acid and direct dyes. Thus they exhaust slowly and produce weak shades with good penetration. Due to the anionic nature of vegetable tannage, the leather so tanned exhibits great affinity for cationic (basic) dyestuffs, to which group belongs Perkin's Mauve, the first synthetic dye.

The available dyes cover a wide range of penetration, and leather technicians are aware of the various factors that influence leather coloring. Nevertheless, there still remain many phenomena connected with dye penetration and levelness that need explaining. It is gratifying to note, however, that in the past few years leather dyeing has attracted the attention of more investigators than in any similar period in the history of the synthetic dyestuff industry. Let us hope that through combined efforts we will learn more about the science of leather coloring.

THE SPRAY OR BRUSH DYEING OF LEATHER

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The surface dyeing of leather in a drum is accompanied by employing controls similar to those used for penetrated shades. However, dyes are selected which have rapid and positive exhausting properties and usually contain large molecular structures and multiple sulfonic groups. The use of dye resists is avoided except where required for leather effects. Dyeing is performed at a lower pH value than for penetrated shades, with the leather definitely on the acid side.

Surface dyeing is frequently done by spray or brush dyeing techniques. This approach is particularly applicable in correcting shades in finishing and in the production of leathers dyed only on the finished side.

Equipment Used in Spray or Brush Dyeing.—Spray dyeing is done with a hand-controlled or automatic gun. The leather is placed either in a vertical or horizontal position for hand spraying.

In the modern finishing machines, the leather is passed through spray booths and drying chambers on horizontal conveyors. The spray guns are

mounted in multiple units on swinging mechanisms synchronized to the movement of the leather to insure uniform dye application. The guns are turned on and off by photo-electric cells which are actuated by the shadow of the leather.

Brush dyeing is accomplished by hand or mechanical devices. Sometimes the color is applied by a brush machine. It is then spread uniformly by workers who swab or brush the leather as it passes on a discharge conveyor belt.

Finish Dyeing of Side Shoe Upper Leather.—The finish dyeing of side shoe upper leather involves three steps. These are: staining, shading of the pigment, and application of resin layers and coloring of the lacquer top coats.

Staining before finishing is done on full grain or "corrected" sides to adjust and to renew the desired shades. "Corrected" side leather is a type in which the grain is partially removed by a sanding operation to obtain a smooth uniform base with a minimum of blemishes. This operation removes the surface color which is replaced by spray or brush dyeing. Sometimes the leather is previously dyed with only a penetrating orange to obtain a natural uniform vegetable-tanned appearance. It is then fully dyed by spraying or brushing with selected colors before finishing. It is generally conceded that full staining before finishing insures colored undertones that characterize the appearance of high-quality leathers. This operation also prevents the occurrence of uncolored scuff marks.

Types of Dyes Used for Staining.—Acid, direct, or chrome dyes are most frequently used for staining and are selected on the basis of several properties.

They must have high tinctorial values, adequate solubility properties in water, and must remain in solution for at least several days. 3% solutions are generally required.

The selected colors should not change in shade when exposed to alkalis, formaldehyde, or other finishing compounds. They should also be adequately fast to light and bleeding. However, these requirements vary considerably, depending on the type of leather. The direct colors are normally superior in these properties to acid and chrome types.

Solubility, penetrating, and spreading properties are improved by the addition of alkalis, solvents, and wetting or dispersing agents. Up to 3% of each of these are used. The ammoniacal compounds appear to be the most effective alkalis. Water-miscible solvents such as acetone, ethyl alcohol, diethyleneglycol monoethylether, and tetrahydro furfurol alcohol are typical solvents. The sulfated alcohols, non-ionic wetting agents, and other dispersing agents are employed to obtain penetration and spreading properties of the dye solution.

Basic dyes are often selected for staining because of their tinctorial value and brightness of shade. They are noticeably less subject to bleeding or

spotting with water than are the acid, direct, or chrome types. They are, however, comparatively inferior in lightfast properties.

The basic dyes are usually applied at 1–2% in ethyl alchol-water solutions. Alcohol is added to increase penetration and to avoid "bronzing". The use of 40–50% of alcohol insures adequate penetration even in dense, full grain leathers. Spirit-soluble dyes are employed for staining when maximum resistance to bleeding in water is desired. These dyes are usually applied in approximately 2% solutions in mixed solvents. Solvents are especially selected to insure proper solubility of the specific dye and to give the desired rate of evaporation.

Shading of Pigment and Resin Finishes with Water-Soluble Dyes.—The second step of finishing side leather involves the application of the pigment and thermoplastic resin layers. Inorganic and organic pigments such as lakes and vat dyes are employed to obtain further coloration and the desired opacity. Several coats containing 15–30% of the pigments are applied, usually by spraying. Up to 1% of the soluble acid, direct, or chrome dye is added to obtain brightness and other shade effects. These finishes contain 20–35% of thermoplastic resins such as the methacrylate or acrylate types in the form of emulsions. This combination, when exposed to heat and pressure, results in a smooth and uniformly coated leather.

Shading of Lacquer Top Finishes with Spirit-Soluble Dyes.—Side leather is frequently given a final finish with solutions of nitrocellulose, alone or in combination with resins. The objectives of this step are to obtain resistance to damage by water and to remove residual tackiness. Spirit-soluble dyes, such as those prepared from treatment of water-soluble dyes, are insoluble in water. They are added to these finishes in concentrations of 1–2% which makes it possible to control the shade and to increase the depth and brilliance. These improvements are possible without excessive bleeding in water.

Use of Dyes in Glazed Calfskin or Goatskin Finishes.—The methods and products used for staining side leather are employed in adjusting the shades while preparing grain calfskin and goatskin for glazed finishes. Similar dyes are added to the glazing compositions. The dyes selected must be resistant to shade change from exposure to alkali, formaldehyde, and heat.

Spray Dyeing of Suede Leathers.—Spray-dyeing techniques are also of value for correcting shades on suede leathers. They are sometimes used for preparation of pastel shades.

Dyeing of White Back Glove Leathers.—Glove leather is frequently colored on one side by brush dyeing on a finish table or by surface dyeing in a drum. In the latter method, the color deposited on the back side is removed

by shaving. The leather is dyed prior to any drying or finishing processes. Rapid-exhausting and non-penetrating direct, developed, or specialty colors are employed. If the colors are applied by brushing, the leather is then transferred to a drum for finishing steps such as rinsing, diazotizing, developing, and fatliquoring.

In conclusion, spray or brush dyeing as outlined is used for preparation or correction of shades on one side of the leathers without disturbing the other. These processes are also valuable in that coloring can be done without rewetting the leather.

DYES AND DYEING PROCESSES FOR SPECIAL PROPERTIES OF COLOR

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The dyes and the methods of dyeing used in leather seldom produce colors that are as fast to light, to soaping, and to solvent cleaning as the colors used in textiles. This is in part due to the nature of leather, to the type of dyes that are commonly used, and to the methods of application. In recent times there has been a serious attempt on the part of the glove, garment, and upholstery tanners to improve the quality of their dyeings. These attempts have met with considerable success in all three fields. It is now possible to produce dyed leathers which compare favorably to textiles in fastness to light, to soaping, and to solvent cleaning. These leathers may be combined in multicolored combinations that can be subjected to normal washing and cleansing operations and to light without fear of stain or loss in color. They can be attained in a nearly complete range of colors.

To achieve these ends the tanner has been obliged to modify both his methods of tanning and his processes of coloring. Dyes have been introduced to the leather industry that are not generally used as leather dyes, and whose use has been largely restricted to textile applications. When we recognize the problems encountered by the dyer in a tannery—problems brought about by the limitations of leather itself—we realize that the goal of producing dyeings of the required fastness properties is exceedingly difficult. Foremost among these limitations are the relatively low temperatures used in leather dyeing (120°–150° F.), the sensitivity of leather to highly alkaline solutions, and the necessity of using a raw material which varies widely in its physical character. Because leather is a derived product, its dyeing properties vary with the nature of the tanning process that produced it. It is difficult to speak of leather except in general terms. Fortunately, the major

portion of all leather is produced by tanning with salts of chromium, and leather thus produced is quite resistant to conditions that would destroy leather made with the natural tannins found in plant extracts. It is this stability of chrome-tanned leather that makes possible the faster dyeing techniques of today.

The leather dyer is concerned not only in producing level dyeings under adverse conditions but also in obtaining a uniform penetration throughout the leather cross-section, especially in suede leather. For this reason fastness properties are frequently subordinated to the more urgent problem of obtaining uniform level dyeings. This has led to the extensive utilization of dyes that are inherently of low fastness but which produce extemely level and uniform dyeings. It must be recognized that the average leather dyer is not a highly trained technician and that he frequently relies upon reasonably fool-proof methods. It is a tribute to the skill and ingenuity of those who produce leather they they are able to produce the excellent products that are available today.

It has been the goal of many in the industry to produce leather dyeings which are comparable in fastness properties to the vat dyes used on textiles. This has been accentuated by the rising demand for leather as articles of clothing which puts it in direct competition with textiles. To meet these requirements it has been necessary to explore several types of dyes and to devise new dyeing techniques to adapt them to leather application. The main groups that have found considerable use are:

1. Direct and chrome dyes
2. Azoic or naphthol dyes
3. Leuco ester vat dyes
4. Sulfur dyes

The direct and chrome dyes are extensively employed in garment leather to produce extemely fast dyeings. Their application involves no change in existing procedures; therefore they are easily adapted to tannery processes. They generally require temperatures of 140° F. or above to insure full chroming of the dyestuff. Because the temperature required approaches the upper limit that is practical in tannery operations, the dyes are generally restricted to the easily chromed types; several are excluded that could be employed at higher temperatures.

As a group the metallizable dyes have excellent fastness especially to dry cleaning procedures. While improved fastness is attained by the use of metallizable dyes, many of the non-metallizable direct dyes yield extremely fast to soap washing by the use of a cationic resin aftertreatment. Because of the extensive range of colors available within this group and the fact that they may be applied to a wide range of tannages, they constitute the major portion of the dyes used for fast dyeing.

The azoic or naphthol dyes are relatively new in leather applications. They have found considerable use in glove and garment leathers, especially where a high resistance to soap washing is required. Except for a few combinations they are much less fast to solvents than the regular chrome or direct dyes. The dyes are applied to leather in the drum as Naphtholates, using slightly more than the theoretical amount of caustic soda necessary to form the Naphtholate. They are exhausted from the solution, in part by the acid in the leather and in part by the addition of acid. The color is developed by adding sufficient diazo base to insure complete coupling. By this method we form essentially a dye pigment in the leather.

The colors produced by these dyes are extremely bright and have a pigment character which permits excellent grain covering. More recently methods have been devised to apply the colors by spray or brushing so as to produce colored grains with uncolored backs. Because of the large number of naphthols available and the fact that they can be coupled with a wide variety of diazo bases, the possible combinations are practically unlimited.

The leuco esters of the vat dyes permit us to apply many vat colors to leather without the difficulties that are encountered in vat dyeing. These dyes are substantive to leather and dye very much as the anionic dyestuffs. They have excellent fastness properties when properly applied and cover almost the complete spectral range. They are extremely bright with outstanding fastness to light and washing. It is both difficult and uneconomical to produce full shades with these dyes. For medium and pastel shades they are unexcelled.

The leuco ester dyes may be applied to chrome leather in the blue or in the crust. Because they dye as anionic dyes the leather is not subjected to alkaline solutions during dyeing. They are developed in acid solution by mild oxidation with sodium nitrite.

These dyestuffs have had considerable application to suede garment leather and glove leather where the accent is on fastness and quality of color.

The sulfur dyes have recently been successfully applied to suede garment leather where high wash fastness is desired. These dyes are essentially a class of vat dyes which are reduced to the leuco state by sodium sulfide. They are applied as the leuco state and are somewhat more substantive to leather than the vat dyes, but have the inherent disadvantage that they require highly alkaline conditions for application. The color of the sulfur dyes ranges from yellow to black but contains no satisfactory reds. It is difficult to obtain satisfactory grain dyeings with sulfur colors chiefly because of the low substantivity of the leuco dye and the rapidity with which it is oxidized during dyeing. Excellent shades of tan, green blue, and grey have been produced by these dyes. Full shades are difficult to obtain.

As with any new process for leather dyeing, where special properties of color are required, changes must be made in tanning procedures to adapt the

leather to the process. Both the sulfur dyes and the naphthol dyes are best applied to crusted leather. The leuco ester vates may be applied to either crusted leather or in the blue. For satisfactory results in coloring with these dyes no vegetable extracts should be present because of the interference in the development of the color. Except for the leuco ester vat dyes, protective measures should be taken to avoid alkaline damage to the leather. This is accomplished in part by modification of the tannage and in part by judicious application of the dyes.

The four methods outlined to a large extent supplement each other. For full shades the chrome and direct colors with resin aftertreatment produce the greatest range of color; the naphthols produce full brilliant shades especially in the reds and oranges; the sulfurs produce excellent tans, greens, and greys—colors that are difficult to produce with naphthols; the leuco ester vats produce excellent pastels and medium shades and have considerable versatility in application. It is thus necessary for the tanner to draw upon members of each class to achieve the full fastness properties desired.

While fastness properties of color is important in many fields of leather, we must constantly bear in mind that no color, however fast, is of value to the leather industry if the process by which it is achieved detracts from leather character. We must constantly bear in mind that we must work within the limitations imposed by the nature of leather itself. Leather gloves, garments, and leather upholstery are luxury items. They hold their place because of an inherent love of all of us for leather. With our present knowledge of coloring operations, it is not reasonable to expect the same fastness in leather that we expect in textiles.

Perkin's synthesis of the first coal tar dye, mauve, was the result of an unsuccessful attempt to synthesize quinine by the oxidation of aniline. Had the structures of aniline and quinine been known to Perkin, he would have realized the impossibility of a successful outcome of the experiment. Had the aniline he used been free from toluidine, no mauve could have resulted.—August Merz, *Encyclopedia of Chemical Technology.*

(*A lack of knowledge is a useful thing.*)

The first coal tar dye (magenta, or fuchsine) was produced in the United States between 1864 and 1869, either in Brooklyn or Albany. First production is variously attributed to August Partz, Thomas Holliday, T. and C. Holliday, and Arthur Bott.—Adapted from Merz in *Encyclopedia of Chemical Technology.*

By the end of 1947, 46 U. S. companies were listed as active producers of dyes. Their output in 1947 was 212 million lbs., valued at 153 million dollars.—August Merz, *Encyclopedia of Chemical Technology.*

Instrument for Measuring Thermal and Elastic Behavior of Hide and Modified Hide Materials

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ABSTRACT

An instrument is described for measuring elongation and contraction of skin and leathers, shrinkage temperatures, stress-strain relationships, and torsional deformation under load. Data obtained on a variety of materials are presented.

INTRODUCTION

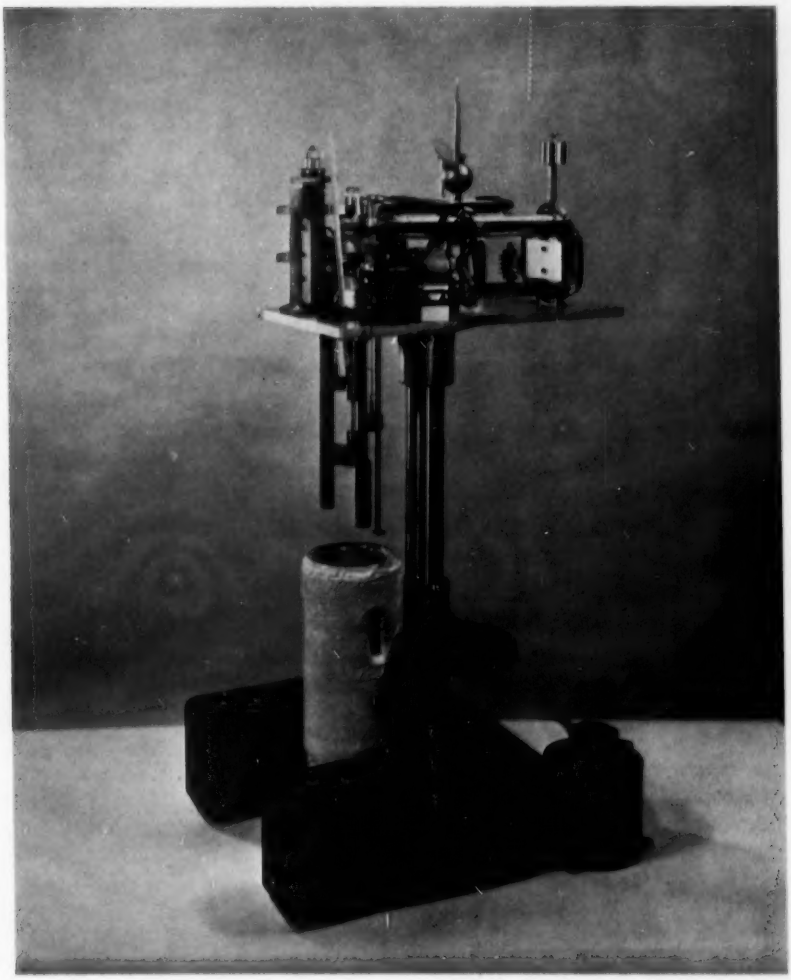
This paper describes an instrument that was designed and constructed to measure quantitatively a variety of the physical constants characteristic of the behavior of hide and chemically modified hide materials. By tests on a single small sample, the instrument permits investigations of: (*a*) elongation and contractile phenomena, (*b*) stress-strain behavior, and (*c*) flexibility in torsion. These studies can be made under various conditions of temperature and in liquid as well as in air. The utility of the instrument in making these investigations is illustrated with observations on cowhide dehydrated with acetone, cowhide tanned with chrome and epoxy resin, and calfskin tanned with canaigre.

Although many instruments for making measurements of this type have been described (1), none of them incorporates all the desired features mentioned above.

APPARATUS AND METHOD

This instrument is purely mechanical in nature and is comprised of two interlinked units which may be operated separately or coordinately. Simply, it incorporates a component for producing and measuring torsion and an adjustable scale and torsion balance for measuring changes in length under constant or variable load. Referring to the photograph and simplified diagram (Figures 1 and 2), one unit consists of a torsion balance, *A*, with a load capacity of 2 kilograms, and a sensitivity of 0.3 gram, in which a spindle, *B*, has been attached to the modified end of the balance beam, *C*. The spindle consists of a cylindrical rod ½ inch in diameter, one end of which has been transformed into a jaw, *D*, for gripping the upper end of the specimen, *Y*. The lower jaw, *D'* is attached to a screw-operated sliding bar, *E*, ½ inch

*One of the laboratories of the Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture.



Courtesy of U.S.D.A. Photo by M. C. Audsley.

FIGURE 1.—Instrument for measuring thermal and elastic properties of hide and leather.

square, by means of an adjustable jacket clamp, *F*. Vertical displacement of the sliding bar is produced by turning a screw by means of a knurled knob, *H*, at its end. The amount of this displacement may be read to 0.001 inch from a scale, *I*, equipped with a vernier. Position of the lower jaw, *D'*, may be changed independent of the scale by loosening the jacket clamp, *F*, and

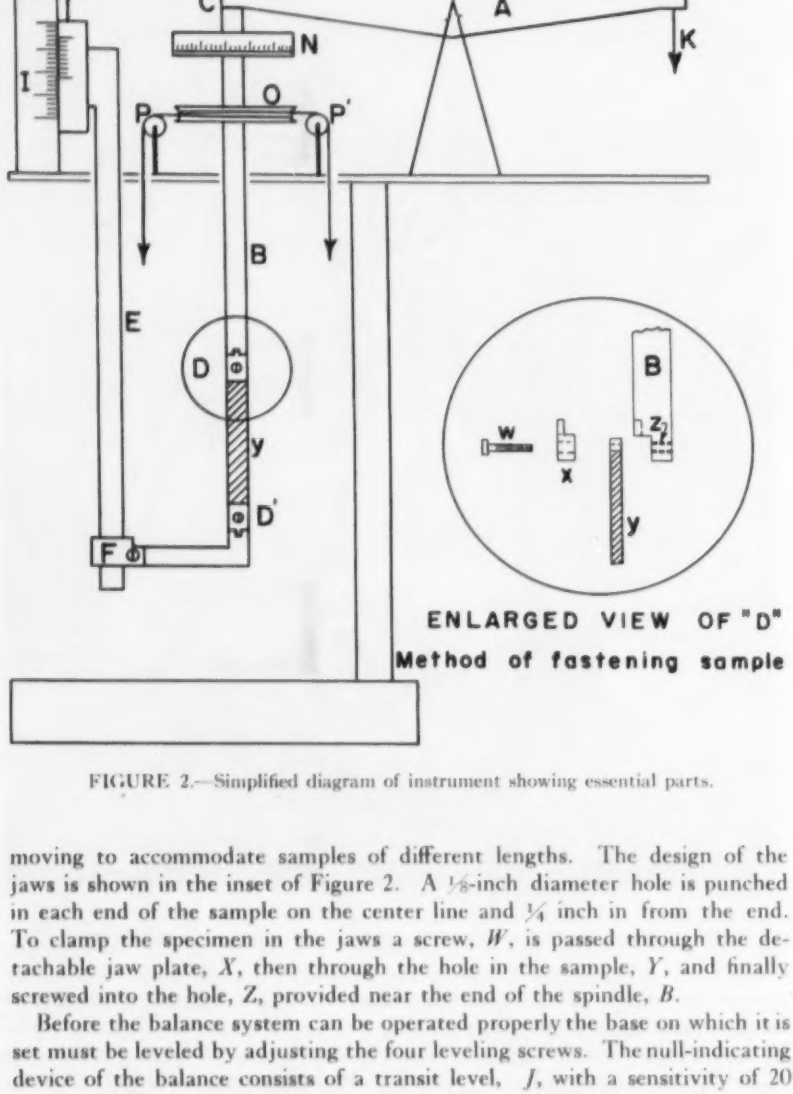


FIGURE 2.—Simplified diagram of instrument showing essential parts.

moving to accommodate samples of different lengths. The design of the jaws is shown in the inset of Figure 2. A ⅛-inch diameter hole is punched in each end of the sample on the center line and ¼ inch in from the end. To clamp the specimen in the jaws a screw, *W*, is passed through the detachable jaw plate, *X*, then through the hole in the sample, *Y*, and finally screwed into the hole, *Z*, provided near the end of the spindle, *B*.

Before the balance system can be operated properly the base on which it is set must be leveled by adjusting the four leveling screws. The null-indicating device of the balance consists of a transit level, *J*, with a sensitivity of 20 seconds. When the sample is placed in position, and all the above adjustments

are made, the system operates as follows: A load placed on the free end, *K*, of the balance produces elongation of the sample which in turn causes the balance null-indicator to be off-center. The screw knob is then turned until the level is centered, and the amount of deformation of the sample is read from the scale. When not in use, the balance may be locked in position by means of four grips, whose action is simultaneously controlled by a lever bar,

The torsion unit of the instrument is similar to one described by Clash and Berg (2) and consists of two parallel cylindrical drums, *N* and *O*, one of which is calibrated in degrees and held at zero position by means of a retaining pin (not shown) which fits into a slot on the drum. Attached to the other drum and wound around it both in the same direction are two nylon fishline cords. These cords are passed over two idler pulleys, *P* and *P'*, which are placed at opposite sides of the drum about three inches from it. Equal calibrated weights are then attached to the ends of the cords. The sample to be tested is clamped in the jaws of the instrument as previously described. When the retaining pin is released, the weights fall causing rotation of the drum and spindle which imparts torsional deformation to the sample. The degree of this deformation is measured by direct reading from the calibrated drum, *N*.

OBSERVATIONS

Shrinkage Phenomena.—In investigations of elongation and contractile phenomena, as, for example, in the determination of shrinkage temperature, a sample of hide or leather 2½ inches long and ¼ inch wide is clamped in the instrument and a 10-gram axial load is applied in tension in order to take up any slack in the sample. The length-adjustment screw is turned until the balance-level indicator is centered, then the scale is read. A Dewar flask containing the immersion medium is set in place on a stand so that sample, heater, stirrer, and thermometer are all immersed. When the sample is immersed in the medium, a resetting of the length-adjustment screw is usually required to compensate for the initial swelling. The screw should be repeatedly reset, with a reading after each resetting, until no further changes in the length of the sample take place. Heating and stirring are then initiated. The rate of heating is regulated by means of a variable transformer. The rate of heating chosen for hide materials was approximately 1°C. per minute for reasons which will be discussed later. The change in length is measured at each desired temperature. The behavior of the sample on cooling may be determined by adding ice or solid carbon dioxide to the liquid medium and following the same procedure as on heating.

Figure 3 shows variation in length with temperature change for *A*, a sample of split cowhide which had been brought to the isoelectric point and then dehydrated with acetone; *B*, a sample of canaigre-tanned calfskin; and *C*, chrome-tanned split cowhide. Upon immersion in tap water, the acetone-

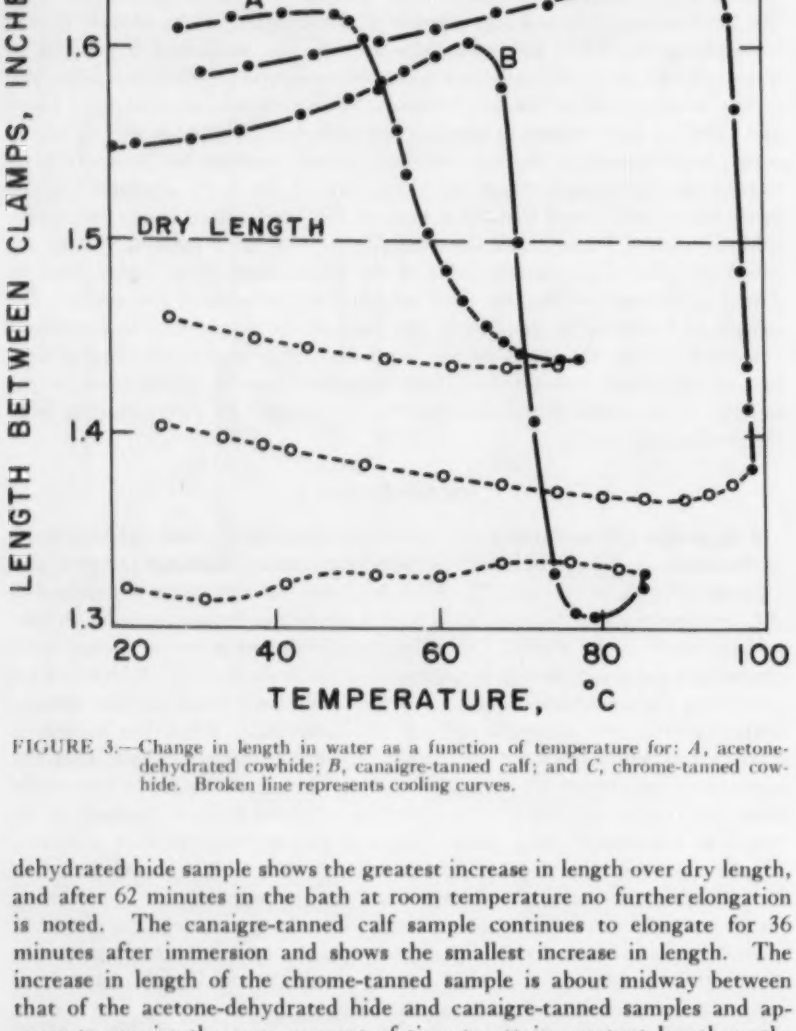


FIGURE 3.—Change in length in water as a function of temperature for: *A*, acetone-dehydrated cowhide; *B*, canaigre-tanned calf; and *C*, chrome-tanned cowhide. Broken line represents cooling curves.

dehydrated hide sample shows the greatest increase in length over dry length, and after 62 minutes in the bath at room temperature no further elongation is noted. The canaigre-tanned calf sample continues to elongate for 36 minutes after immersion and shows the smallest increase in length. The increase in length of the chrome-tanned sample is about midway between that of the acetone-dehydrated hide and canaigre-tanned samples and appears to require the same amount of time to attain constant length as the latter. When no further change in length at room temperature occurs, heating is initiated. All the samples exhibit a further increase in length up to the point where shrinkage occurs, the amount of this increase depending upon the

chemical treatment of the sample. The shrinkage temperature, *Ts*, is considered to be the temperature corresponding to the point at which the first decrease in length is observed. The *Ts* values obtained fell in the expected order, that is, chrome-tanned hide, 94°C; canaigre-tanned calf, 65°C; and acetone-dehydrated hide, 49°C. The values obtained for the samples of canaigre-tanned calf and acetone-dehydrated hide are rather low. On cooling

TABLE I

EFFECT OF HEATING RATE ON TEMPERATURE AND RANGE OF SHRINKAGE OF ACETONE-DEHYDRATED COWHIDE

Heating Rate, °C/min	Ts, °C.	Shrinkage Range, °C.
2	55	55–62
1	55	55–60
0.2	54	54–56

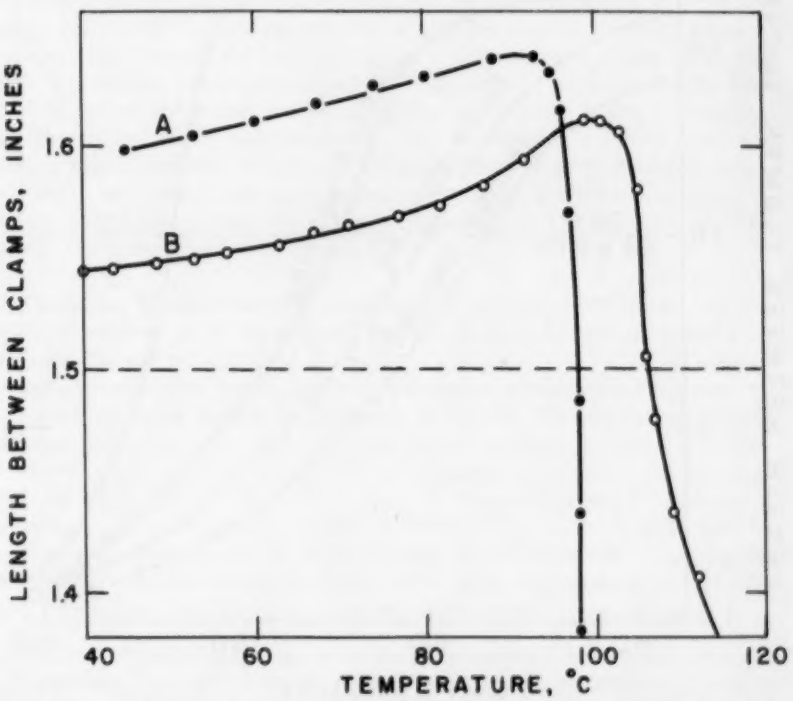


FIGURE 4.—Change in length as a function of temperature for chrome-tanned cowhide; *A*, in tap water pH 7; and *B*, in 25% water 75% glycerol solution.

at a rate of 2°C. per minute, the shrunken samples of acetone-dehydrated hide and chrome-tanned cowhide exhibit a slight increase in length, while the length of the canaigre-tanned sample remains essentially unchanged.

To show the effect of heating rate on the *Ts* value and rate of shrinkage, three test specimens were cut adjacent to each other from another preparation of acetone-dehydrated hide. These specimens were all tested in distilled water by the method just described, except that each was heated at a different rate. The results are shown in Table I. From these results we may conclude that shrinkage temperature is practically independent of heating rate, at least at rates below 2°C. per minute with only the 10-gram load acting on the sample. The shrinkage range, however, varies significantly with heating rate.

In comparison with values obtained by standard methods the values presented in Table I are approximately 5°C. low. This is probably due in part to

FIGURE 5.—Change in length in water as a function of temperature of cowhide tanned with epoxy resin.

the sensitivity of this instrument which detects changes in length as small as 0.001 inch and also the small load (10 grams) used compared to 100 grams for some of the other methods.

The effect of different liquid media on similar samples of chrome-tanned cowhide may be seen in Figure 4. The values for curve *A* are obtained in tap water while those for curve *B* are obtained using glycerol containing 25% water. The sample tested in tap water shows a much greater increase in length on immersion, and the *Ts* value obtained in the glycerol solution is 8°C. higher than that obtained in water.

An example of reversible shrinkage behavior is shown in Figure 5, in which length is plotted as a function of temperature for a sample of split cowhide tanned with epoxy resin (3) and tested in tap water. After immersion in water at 28°C., the sample increases in length for 12 minutes. However, on heating, no essential increase in length occurs; in fact a slight decrease is observed as the shrinkage temperature is approached. At a temperature of 78°C. a rapid decrease in length begins which continues until the boiling point of the water is attained. On cooling at a rate of 2°C. per minute, the sample length increases rapidly until the sample is cooled to a temperature of approximately 46°C.; thereafter a more gradual increase takes place. At the end of the first cooling period, the sample length at 28°C. (not shown) is the same as the length attained at the start of the heating. On heating a second time, the sample begins to shrink at about 58°C., approximately 20°C. below the original shrinkage temperature of the sample. Although not shown in Figure 5, at the end of the second cooling cycle the sample is 0.35 inch shorter than at the beginning of the first heating cycle.

Torsional Measurements.—In determining torsional deformation under load—a measure of the flexibility—the sample is, as before, subjected to a 10-gram "straightening" load in tension. The balance is locked in position to maintain constant length, and the appropriate torsional load is applied by releasing the retaining pin as previously described. The amount of torsional deformation is read from the calibrated drum. In these experiments torque-loads of 0.0125 to 0.03 inch-pound are employed to produce deformations varying from 100° to 500°. Between torsion measurements the balance is unlocked, and the change in length is adjusted as previously described, to maintain constant tension on the sample during the entire test. Applying the formula relating dimensions of sample, torque-load, and degree of deformation given by Clash and Berg (4), a torsional modulus may be calculated.

Figure 6 shows a graph in which apparent torsional modulus in water is plotted as a function of temperature. These values were obtained simultaneously with those reported in the curves shown in Figures 3 and 5, and therefore they correspond to the same samples. These values are calculated

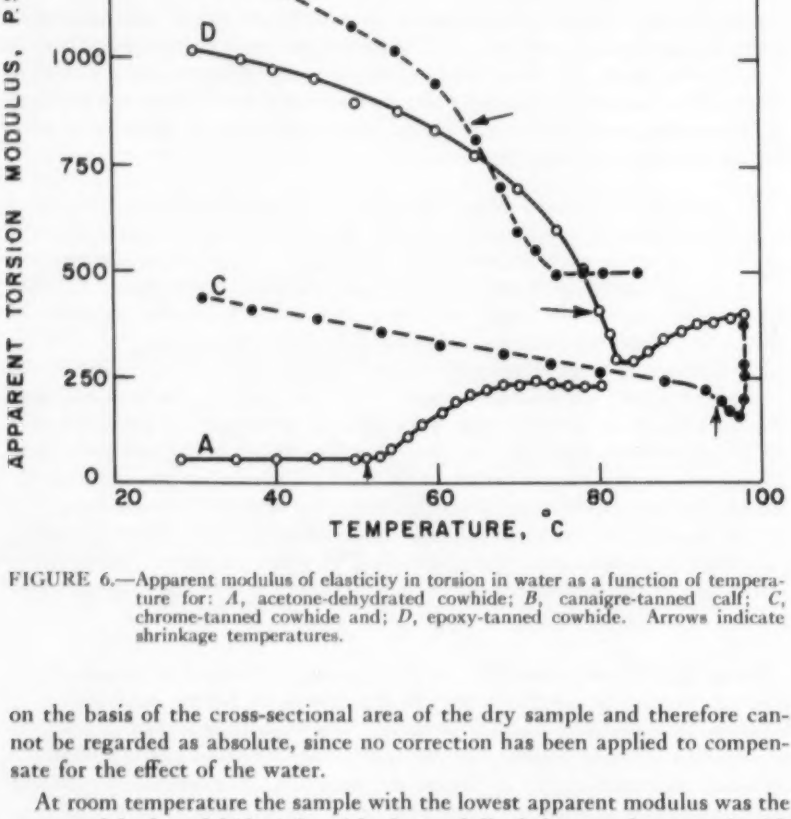


FIGURE 6.—Apparent modulus of elasticity in torsion in water as a function of temperature for: *A*, acetone-dehydrated cowhide; *B*, canaigre-tanned calf; *C*, chrome-tanned cowhide and; *D*, epoxy-tanned cowhide. Arrows indicate shrinkage temperatures.

on the basis of the cross-sectional area of the dry sample and therefore cannot be regarded as absolute, since no correction has been applied to compensate for the effect of the water.

At room temperature the sample with the lowest apparent modulus was the acetone-dehydrated hide (*A*), with the moduli of the samples tanned with chrome (*C*), epoxy resin (*D*), and canaigre (*B*), being approximately 7, 20, and 26 times as great, respectively. These values appear to show that stiffening occurs on tanning and that the stiffness of the wet samples seems to vary with the type of tannage. For the tanned materials the modulus values exhibit a gradual decrease with increasing temperature in the initial portion of the curves, while the modulus of the acetone-dehydrated hide remains constant. When the shrinkage temperature is attained, the tanned samples all show a rapid decrease in apparent modulus. The acetone-dehydrated sample again behaves differently in that shrinkage causes an increase in modulus. The final portions of the curves are all of a different nature: the chrome-

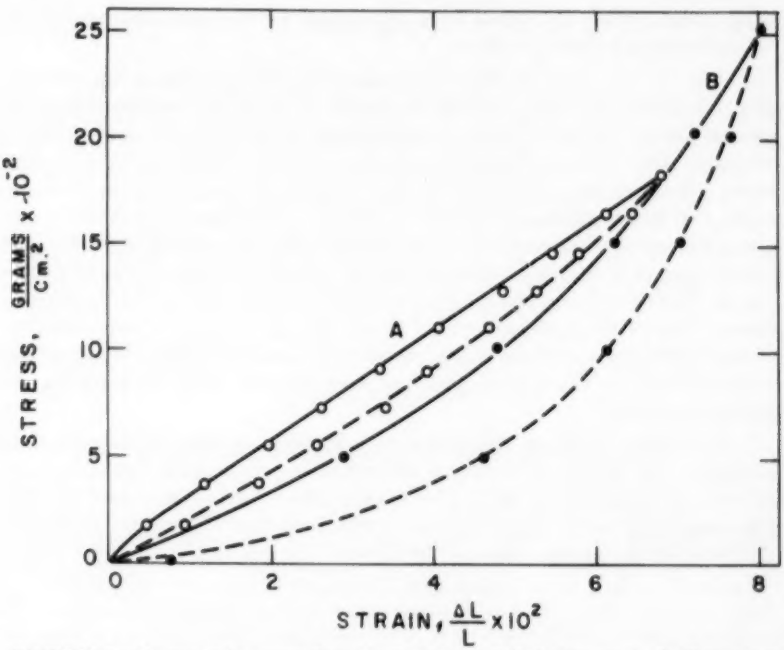


FIGURE 7.—Stress-strain curves for: *A*, cowhide shrunk 3 minutes in boiling water; and *B*, acetone-dehydrated cowhide as received. Determinations were made in distilled water at 25°C.

tanned hide showing a sharp increase and the epoxy-resin-tanned hide, a slight increase, while the canaigre-tanned calf and acetone-dehydrated hide remain constant.

Stress-Strain Measurements.—The instrument may also be employed in measuring the stress-strain behavior of hide and leather samples. This determination is made by mounting the sample in the jaws of the instrument, putting the bath in place, and applying loads to the free end of the torsion balance. The load is increased in equal increments, and the change in length produced by each increment of load is measured by means of the scale and vernier. Figure 7 shows an example of a graph obtained from this type of measurement on two samples of acetone-dehydrated cowhide. Curve *B* shows values for isoelectric acetone-dehydrated hide before shrinking, and curve *A*, values for hide after shrinking in boiling water for three minutes. Both specimens were tested in distilled water at room temperature, and conditioning loads of 1000 and 710 grams respectively were first applied in order to remove most of the nonrecoverable elongation. The cross-sectional areas

used in calculating the stress were determined by the method employed by Wiederhorn and Reardon (5).

The shrunken material shows an essentially linear stress-strain relationship on increasing load, and the modulus of elasticity obtained was 425 pounds per square inch. On stepwise removal of the load a hysteresis loop is obtained. On the other hand, the stress-strain curve of the unshrunk sample shows initially a large nonlinear increase in strain per unit stress in the stress range of 0 to 500 grams per square centimeter. At stresses from 500 to 1000 grams per square centimeter the stress-strain behavior parallels that observed for the shrunken sample, and thus the modulus is the same for both in this region. On further increase in stress, above 1500 grams per square centimeter, the modulus of the unshrunk material increases by a factor of two over that of the middle portion of the curve. It may be noted that the modulus values reported here are of the same order of magnitude as those obtained by the torsion method.

It is possible to follow the course of a tanning reaction *in situ* on small specimens by measuring torsional deformation, stress-strain behavior, and changes in length while tanning is taking place. Additional uses for this instrument are found in evaluation of torsional and contractile properties of other polymeric materials such as rubbers and plastics.

SUMMARY

An instrument is described which was designed and constructed in this laboratory for the purpose of investigating hydrothermal and elastic properties of hide and modified hide materials. The apparatus incorporates a torsion-producing and-measuring component and an adjustable scale and torsion balance for measuring changes in length under variable load when necessary. The measurements can be made as a function of temperature in air or liquid media as desired. The apparatus has the following qualities: it is versatile and measures fundamental properties over a useful range of temperature; it is simple in operation, relatively inexpensive in cost, and suitable for routine use in industry; and it requires specimens which are easy to prepare. Methods for measuring shrinkage temperature and amount of shrinkage, effects of tanning on torsional stiffness, and stress-strain behavior before and after shrinkage are discussed, and examples of data obtained are given.

ACKNOWLEDGMENTS

We are grateful to Dr. E. M. Filachione and his colleagues of the Hides, Tanning Materials and Leather Section of this Laboratory for preparation of all samples mentioned herein and to D. R. Killen for making many of the reported measurements.

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INTERNATIONAL WOOL RESEARCH CONFERENCE

At an international conference held in Australia, in August and September of 1955, about 150 papers were presented on the biology, physics, chemistry, and technology of wool. Many of these papers appear to have a bearing on the problem of the mechanism of unhairing. Some of the more important findings disclosed at this conference were reviewed at a seminar held in New York, in November, 1955, under the auspices of the Wool Bureau and the Textile Research Institute. Talks were given by J. H. Dillon (General Remarks on the Conference), Gerald Laxer (Morphology and Chemical Modification), Harold P. Lundgren (Highlights of Papers on Physical and Protein Chemistry), and J. Menkart (Biology and Manufacture). These addresses, as well as a complete list of the papers presented at the conference, were published in *Textile Research Journal*, **26,** 361–84 (1956). The original papers are to be published in book form late in 1956.

Philosophy of work simplification is that difficult problems can be reduced to simple steps and that management can control efficiency of operation by stimulating employees to be constantly alert for possible improvements, according to Alan H. Morgenson. Presenting his views before the American Materials Handling Society Technical Sessions at Cleveland, Morgenson said that automation and electronic devices are not going to help the small shops. One must produce tremendous quantities and be frozen as to type of product before going into real automation. The small shop cannot justify the investment involved. "It is the people you have working for you now who will make the saving," Mogenson says. —*Chemical Engineering News*, Aug. 6, 1956.

A THOUGHT FOR THE MONTH

When coloured leathers are being used, they are usually at the same time being exposed to light—otherwise they would not be seen.

—*J. Soc. Leather Trades' Chemists*, June, 1956.

Zirconium Tannage. VII—Direct Utilization of Insoluble Zirconium Derivatives*

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ABSTRACT

Experiments show that zirconium tannage can be effected by treating pelt with various insoluble zirconium compounds in the presence of sulfuric acid and neutral salts. One of these compounds—sodium zirconium silicate—has been tested on a commercial scale and possesses certain advantages over the commercial zirconium tanning compounds now in use.

INTRODUCTION

In the early development of zirconium tannage it was natural that attention should be directed to the use of soluble salts of zirconium. Both normal zirconium and basic zirconyl salts are taken up by pickled skin even at low pH values. The tanning is completed by washing or neutralizing the leather before applying the customary fatliquors (1). The minimum amount of normal zirconium sulfate necessary for tannage is that equivalent to 3% ZrO_2 based on the drained pickled weight of skins, but better results are obtained with 5% ZrO_2. Basic zirconyl sulfate is as effective as normal zirconium sulfate, which indeed hydrolyzes partially in solution to form a basic sulfate. The sulfate was found to be more effective than zirconyl chloride or nitrate, so it was adopted for development and subsequently prepared in a dry form as a technical product for tannery use. Practical procedures for tanning with this material were outlined by Turley and Somerville with specific recommendations for the preparation of white leather (2); these were later revised and brought up to date by Somerville and Turley (3). It was shown that this material could be applied in conjunction with chrome salts to produce many varieties of colored leathers (4). During the war years, when the country was threatened with a possible shortage of chrome, this was of national importance. A study of the complex sulfates of zirconium was made by Somerville and Rau (5), and while no final conclusion on the mechanism of tannage was reached, some evidence was advanced on the nature of the complex sulfates present and on the ionic character of the zirconium in the tanning sulutions. Additional information on the theory of zirconium tannage was provided by the stimulating work of Chambard and Lasserre at the French Tanning School (6), while on the practical side the development of a cheaper tanning salt was promoted in the same country by Paquet (7).

*Presented at the Fifty-second Annual Meeting, Mackinac Island, Michigan, June 19, 1956.

We recently had occasion to carry out some experiments on insoluble zirconium derivatives and have found it possible under favorable conditions to use some of these directly in tanning.

EXPLORATORY TANNING TESTS

Hydrated Zirconium Dioxide.—A solution of zirconium sulfate was treated with an excess of ammonia, and the precipitate was washed until free from sulfates. On removing excess water by suction the gelatinous residue showed the composition $ZrO_2 \cdot 25\ H_2O$. A small piece of pickled calfskin was brought to the isoelectric point, washed, drained and then shaken in 200% of a 6 % solution of sodium sulfate. Enough of the hydrated oxide to correspond to 5 % ZrO_2 was added, and shaking continued for 144 hours. No appreciable tannage took place; the final shrinkage temperature was only 135°F., and the skin dried out hard and undertanned.

It was found, however, that when this experiment was repeated with the addition of increasing amounts of dilute sulfuric acid, in the presence of the calfskin and at room temperatures, considerable tannage took place, and values of up to 208° F. were secured for shrinkage temperatures. These pieces of skin were finished, and those tanned in the range of 0–50% basicity had good appearance and leather quality. Comparative tests using chromic hydroxide were also carried out, and similar, though not identical, results obtained. These observations, published by Somerville in 1954 (8), showed clearly that it was possible to effect tannage beginning with insoluble hydrated zirconia by acidifying directly in contact with raw skin at room temperature. This effect is shown in Table I and Figure 1, where the shrinkage temperatures attained in 24 and 144 hours are plotted against the amount of acid given. Both curves show the same trend, but the 24-hour values are markedly lower in the tanning range, showing that this reaction takes place slowly at room temperature. By longer shaking, however, a good result was obtained.

TABLE I

TANNING DEPICKLED CALFSKIN BY ADDING H_2SO_4 TO HYDRATED ZIRCONIA (5% ZrO_2)

% H_2SO_4 *	% Basicity	pH (spot)	T_s, °F. 24 hr.	T_s, °F. 144 hr.
0.0	100	6.5	130	137
0.8	90	5	130	137
1.6	80	4	130	137
2.4	70	3.5	130	137
3.2	60	3	130	137
4.0	50	2.5	130	157
6.0	25	2	150	205
8.0	0	1.75	192	210

*All percentages are based on drained pickled weight.

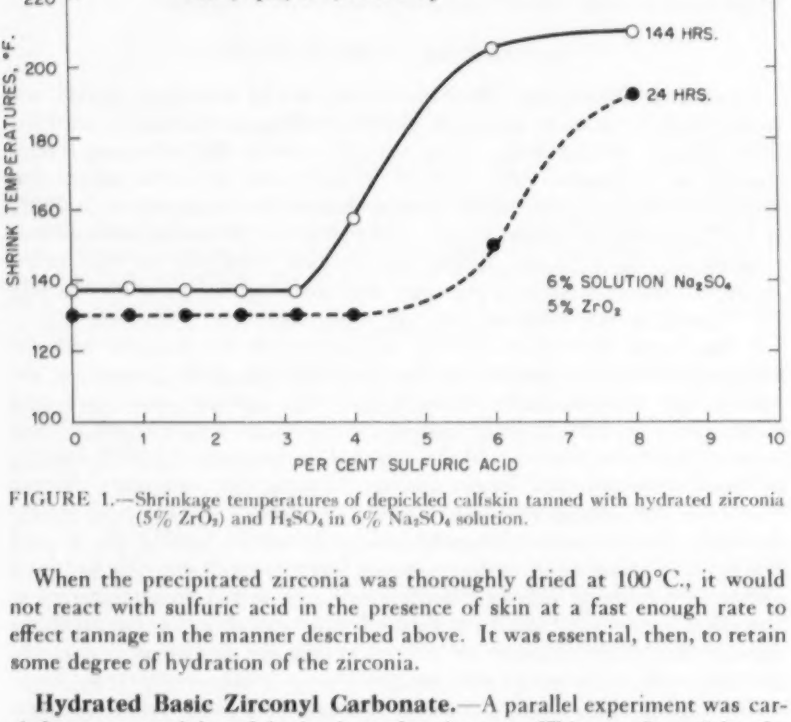

FIGURE 1.—Shrinkage temperatures of depickled calfskin tanned with hydrated zirconia (5% ZrO_2) and H_2SO_4 in 6% Na_2SO_4 solution.

When the precipitated zirconia was thoroughly dried at 100°C., it would not react with sulfuric acid in the presence of skin at a fast enough rate to effect tannage in the manner described above. It was essential, then, to retain some degree of hydration of the zirconia.

Hydrated Basic Zirconyl Carbonate.—A parallel experiment was carried out on precipitated basic zirconyl carbonate. This was formed by the addition of enough soda ash to a solution of zirconium sulfate to give pH 5, the precipitate being washed free from sulfates, and excess water being removed by pressing out on the filter. This product may vary somewhat in composition, but when prepared by us in this way it showed 75% basicity on the Schorlemmer scale. It did not prove to be so effective in tanning as hydrated zirconia; even on shaking for 144 hours with adequate acidification the best shrinkage temperature obtained was 180°F. This seemed to be due in part to excessive precipitation on the surface and incomplete penetration. By the use of 50% more zirconium salt (7.5% ZrO_2), a better result was obtained. This is shown in Table II and Figure 2. The finished pieces tanned in the range of 0–50% basicity had a good appearance and leather quality. In practical tanning it is customary to begin with pickled rather than depickled skin, and under these conditions a shrinkage temperature of over 200°F. was obtained in a few hours.

TABLE II

TANNING DEPICKLED CALFSKIN BY ADDING SULFURIC ACID TO BASIC ZIRCONYL CARBONATE

% H_2SO_4*	% Basicity	pH (spot)	Ts. °F. 24 hr.	Ts. °F. 144 hr.
		5% ZrO_2 given		
0.0	75	4.5	140	145
1.0	62.5	4	140	145
2.0	50	3.25	150	170
3.2	35	2.5	155	178
4.0	25	2	160	180
6.0	0	1.5	160	180
		7.5% ZrO_2 given		
0.0	75	4.5	140	145
1.5	62.5	4	145	147
3.0	50	3.25	170	190
4.8	35	2.5	185	197
6.0	25	2	190	200
9.0	0	1.5	195	200

*All percentages are based on drained pickled weight.

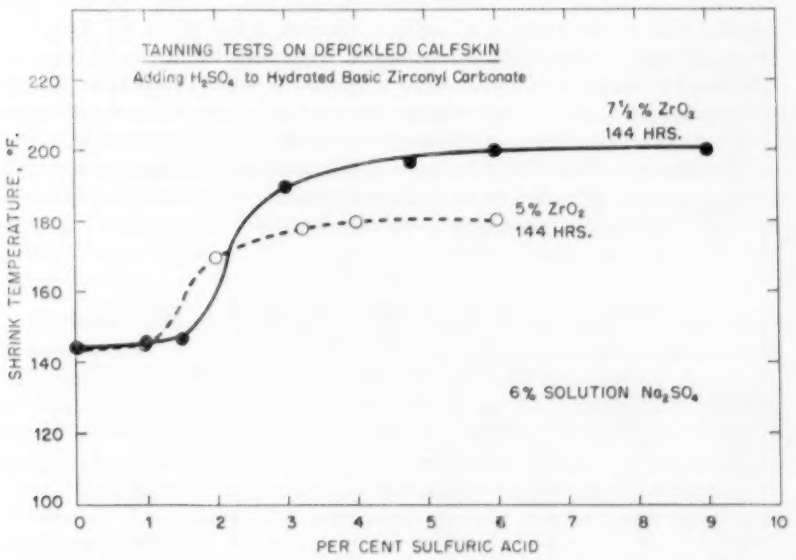

FIGURE 2.—Shrinkage temperatures of depickled calfskin tanned with hydrated basic zirconyl carbonate and H_2SO_4 in 6% Na_2SO_4 solution.

Sodium Zirconate.—In our first paper on zirconium tannage (1), recognition was given to zirconates, but these were set aside as of little interest in tanning on account of their poor solubility. On adding zirconates to water some hydrolysis occurs leading to the formation of insoluble hydrated zirconia and caustic soda:

$$Na_2ZrO_3 + 2H_2O \rightleftarrows ZrO_2(H_2O)_x + 2NaOH$$

In view of the reactivity of hydrated zirconia with acid at room temperatures it seemed of interest to try the addition of sulfuric acid to sodium zirconate. This should neutralize the caustic soda formed by hydrolysis and in addition convert the hydrated zirconia to a water-soluble basic sulfate.

Sodium zirconate was prepared by heating zirconium oxide with soda ash at 1000°C. until a good sintering reaction occurred. The residue was ground to a fine powder which by analysis showed 57% available ZrO_2 (in theory 66%). Tanning tests were carried out on depickled calfskin in the same way as for hydrated zirconia in the presence of a 6% solution of sodium sulfate, and giving the equivalent of 5% ZrO_2. Higher amounts of sulfuric acid were necessary since one mole was required to neutralize the alkali present.

$$Na_2ZrO_3 + 2H_2SO_4 \rightleftarrows Zr(OH)_2SO_4 + Na_2SO_4 + H_2O \qquad (I)$$

However, even at basicities equal to those used for hydrated zirconia the maximum shrinkage temperature obtained was only 160°F. It was then recalled that in the analysis of sodium zirconate a low result for ZrO_2 was obtained when it was broken down by heating with sulfuric acid, but the calculated ZrO_2 value was more nearly approached when it was treated with hydrochloric acid. Accordingly the tanning tests were repeated in the presence of a 5% solution of sodium chloride instead of 6% sodium sulfate. The results, shown in Table III and Figure 3, indicate that good tannage occurred in the same basicity range as for hydrated zirconia. Again the pieces tanned in the 0–50% basicity range gave good white leather.

TABLE III

TANNING DEPICKLED CALFSKIN BY ADDING SULFURIC ACID TO SODIUM ZIRCONATE (5% ZrO_2)

		Tanned in 6% Na_2SO_4 Solution			Tanned in 5% NaCl Solution		
% H_2SO_4*	% Basicity	pH (spot)	T_s, °F. 24 hr.	T_s, °F. 144 hr.	pH (spot)	T_s, °F. 24 hr.	T_s, °F. 144 hr.
0.0	100	10+	135	135	8.5+	135	135
4.0	75	6.5	140	150	6.5	140	140
6.4	60	3.25	140	150	3.5	145	145
8.0	50	2.5	150	155	2.5	150	197
10.0	25	1.75	150	157	1.5	190	204
12.0	0	1.5	150	157	1.25	200	204

*All percentages are based on drained pickled weight.

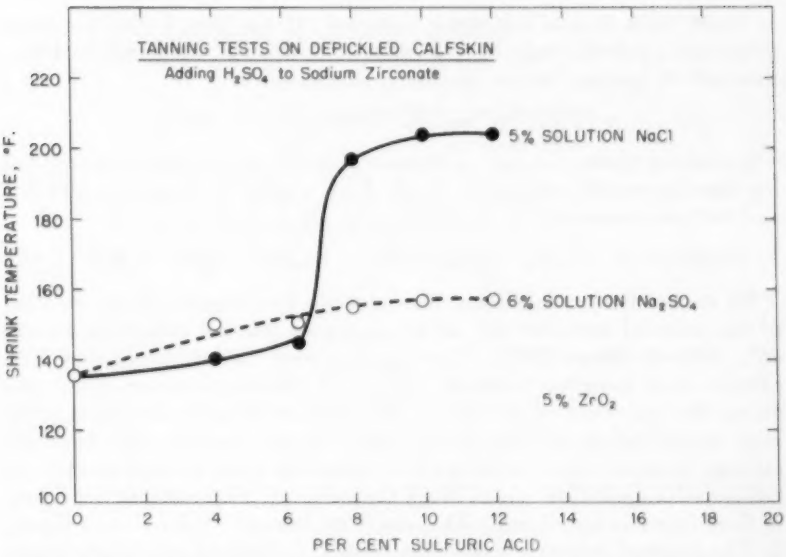

FIGURE 3.—Shrinkage temperatures of depickled calfskin tanned with sodium zirconate (5% ZrO_2) and H_2SO_4 in (*a*) 6% Na_2SO_4 solution; (*b*) 5% NaCl solution.

In actual practice this method of tannage would have no advantage over the use of hydrated zirconia; indeed it requires double the amount of sulfuric acid. However, one important natural source of zirconium is the ore, Zirkite, found in large deposits in Brazil. The zirconium is present mainly as the oxide or as a mixture of oxide and silicate, usually in association with iron impurities. An ore of this composition could not be utilized directly in tanning, but by conversion of the oxide to sodium zirconate as described above, it should be possible to secure the reactivity toward acid necessary for conversion of skin to leather.

Sodium Zirconium Silicate.—The three examples outlined above show that it is possible to begin with water-insoluble zirconium derivatives and react them with acid in presence of raw skin at ordinary temperatures in such a way as to produce a satisfactory tannage. These are of interest in expanding the range of methods of zirconium tannage, but they are unlikely to lead to any marked reduction in the cost of a commercial product. A suggestion by the junior author opened up a new approach to this problem by exploring the possibility of utilization of sodium zirconium silicate in a similar manner to sodium zirconate.

Sodium zirconium silicate can be produced in a relatively simple manner from zirconium silicate, the most widespread zirconium ore, found as deposits

in beach sands in this and other countries. It has been known for many years that a rich ore, reduced to a fine state of division, can be sintered with soda ash to produce sodium zirconium silicate (9):

$$ZrSiO_4 + Na_2CO_3 \rightarrow Na_2ZrSiO_5 + CO_2$$

The resulting product is very much more reactive than zirconium silicate and has been previously reported to break down readily by treatment with hot acid to form water-soluble zirconium salts and free silica:

$$Na_2ZrSiO_5 + 2H_2SO_4 \rightarrow Zr(OH)_2SO_4 + Na_2SO_4 + SiO_2 + H_2O \qquad (II)$$

We studied the methods recommended in the literature for the preparation of this material and were able to secure a good product containing around 46% ZrO_2 (in theory 50%). Tanning tests were carried out on depickled calfskin in the same way as above, using a 6% solution of sodium sulfate and giving the equivalent of 5% ZrO_2. The amounts of acid required were the same as with sodium zirconate, but it was found that at comparable basicities tannage occurred much more readily, indicating good breakdown even in sodium sulfate solution. In 24 hours the shrinkage temperatures were close to those found at equilibrium. The results are shown in Table IV and Figure 4. The pieces of skin were thoroughly washed, fatliquored, and dried, giving good white leather in the tanning range of 0–50% basicity.

The speed of reaction of sodium zirconium silicate with acid at room temperature is compared directly with hydrated zirconia in Figure 5. At a basicity of 50% the latter showed a shrinkage temperature of only 130°F. in 24 hours, in contrast to 190°F. for sodium zirconium silicate; while at a basicity of 25%, the figures were 150° and 197°F. respectively. The difference was very small at a basicity of 0%. However, this faster reaction of sodium zirconium silicate is extremely important in considering the possible application of reactions of this type in practical tanning.

TABLE IV

TANNING TESTS ON DEPICKLED CALFSKIN ADDING H_2SO_4 TO SODIUM ZIRCONIUM SILICATE (5% ZrO_2)

% H_2SO_4*	% Basicity	pH (spot)	T_s, °F. 24 hr.	T_s, °F. 144 hr.
0.0	100	7	140	145
4.0	75	4	150	165
6.4	60	3.5	170	195
8.0	50	3	190	205
10.0	25	1.75	197	206
12.0	0	1.5	197	206

*All percentages are based on drained pickled weight.

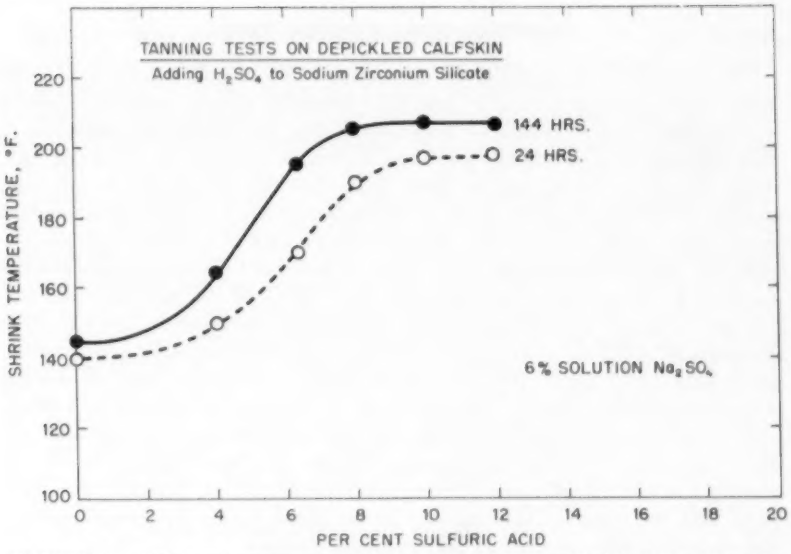

FIGURE 4.—Shrinkage temperatures of depickled calfskin tanned with sodium zirconium silicate (5% ZrO_2) and H_2SO_4 in 6% Na_2SO_4 solution.

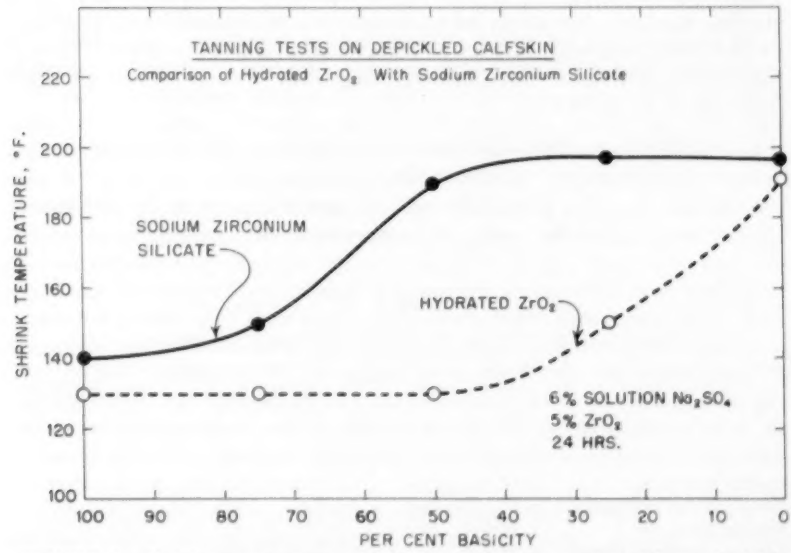

FIGURE 5.—Shrinkage temperatures of depickled calfskin tanned at different basicities with (*a*) hydrated zirconia and (*b*) sodium zirconium silicate (both 5% ZrO_2) and H_2SO_4 in 6% Na_2SO_4 solution for 24 hours.

CONFIRMATORY TANNING TESTS

The preceding series of curves may seem to be of only academic interest because the tanning process at first sight seems to require six days to attain equilibrium. But it should be emphasized that the conditions employed in this theoretical approach are not those normally utilized in zirconium tannage. It has been recognized for many years that the skins should be adjusted initially to a low pH rather than to the isoelectric point in order to insure fast penetration of the tanning salt. Accordingly, enough of each insoluble derivative was prepared to tan an 8-inch strip of lime-split steerhide grain pickled to pH 1.5. These pieces were opened up in 200% of 5% salt solution, and enough of the zirconium derivative was added dry to correspond in ZrO_2 to 20% Zircotan N*. Dilute sulfuric acid was added to the solution to give a calculated basicity of about 40% for the zirconium salt added, and drumming was continued for 6 hours. The shrinkage temperatures obtained in 4 hours and overnight in the acid condition, and also after neutralizing next day are shown in Table V. After fatliquoring, crusting, and working up, the leather quality was good in all cases. The penetration of tanning material was complete, and had occurred very rapidly except in the case of hydrated zirconia, and even this was satisfactory on tanning overnight.

These confirmatory tests indicated that this approach to zirconium tannage might with advantage be followed up on a practical scale. Consideration of the four insoluble derivatives led to the selection of sodium zirconium silicate as the most promising because of its greater availability, relative ease of preparation, and faster breakdown by dilute acid. Two important questions had then to be answered:

a. Would it be feasible under tanning conditions to add the large amount of acid necessary to solubilize the zirconium?

b. Would the silica formed be inert, or would it prove to be detrimental or beneficial to the quality of leather produced?

TABLE V

TANNING TESTS ON PICKLED STEERHIDE GRAINS

	After 4 hours		Overnight		After Neutralizing	
	pH	T_s, °F.	pH	T_s, °F.	pH	T_s, °F.
Zircotan N	1.5	202	1.5	205	4.5	206
Hydrated zirconia	1.25	140	1.25	197	4.5	203
Basic zirconyl carbonate	1.25	202	1.25	204	4.5	204
Sodium zirconate	1.25–1.5	202	1.25–1.5	205	4.5	206
Sodium zirconium silicate	1.25–1.5	202	1.25–1.5	205	4.5	206

*A basic zirconium sulfate, the composition of which has been published (4).

Tanning tests carried out on a laboratory scale and in our experimental tannery showed that by suitable dilution the addition of sulfuric acid took place smoothly. Depending on the basicity desired, the amount ranges from 75 to 85 % of the sodium zirconium silicate given. Since the latter may vary from 10 to 15% of the weight of pickled skin, the acid required may be about 8–12% of the skin weight. The simplest method of operation was to make up a solution of dilute acid, say 2 lb. per gallon, add the dry zirconium derivative to the skins in a brine solution, and then add enough of the acid solution through the gudgeon while the drum was running. The small amount of heat of neutralization did not raise the temperature of the skins and liquor more than 10–20°F.—an important point to watch. The temperature was easily controlled by varying the volume of liquor used. Once the reaction had taken place the system was not unduly acidic, showing pH values in the same range as with an equivalent amount of Zircotan N. An alternate method of operation which might be preferable under some tannery conditions was to react the sodium zirconium silicate with more dilute acid, say ½ lb. per gallon, out of contact with the skins, and then add this solution, after cooling, to the skins in the tanning drum. Still another possibility was to make a dry mix of sodium zirconium silicate with a dry acid such as niter cake and add this mixture directly to the tanning drum. However, it seemed quite feasible to add dilute sulfuric acid to the zirconium salt in contact with the skins as indicated.

In looking for an answer to the second question we may go back for a moment to Equations I and II comparing the behavior of sodium zirconate with sodium zirconium silicate. The reaction products are exactly the same except for the silica present in the second case. We found that when this reaction is carried out at room temperature the silica is present as water-soluble silicic acid, probably in monomeric form or in a low degree of polymerization. In this state it was readily taken up by the skins under our conditions of tanning. In some instances it was fixed almost quantitatively on neutralization, giving additional tanning or filling action over that obtained with an equivalent amount of zirconium alone. This beneficial effect was more pronounced than that obtained when the same amount of silica was given as insoluble SiO_2, which is the case if such a reacted solution is dried before application to the skins. A search in the literature on silica tannage, supplemented by small-scale laboratory tests, showed that to get the best tanning effect sodium silicate should be added in solution to an excess of cold, dilute sulfuric acid, then the silica should be fixed in the skins by subsequent neutralization. Our conditions were just those prescribed for silica tannage, so it was obvious why we obtained some benefit from its presence along with the more effective zirconium tannage. Because there has been some criticism of the aging properties of silica-tanned leather, we studied the aging of leathers prepared as described above. Careful rapid aging tests

for short periods at high temperatures, and actual storage at room temperatures for as long as three years, have so far not shown any adverse effect due to the presence of this silica in zirconium-tanned leathers. The presence of silica does necessitate a small adjustment in fatliquor. Hence the answer to this second question is that the presence of silica is on the whole beneficial.

PRACTICAL TANNERY TRIALS

We next proceeded to experiment on a tannery scale. The general procedures followed were those published for application of Zircotan N, substituting an equivalent amount of ZrO_2 in the form of acidified sodium zirconium silicate. A number of experiments were successfully carried through on a small scale and on full-size drum loads. Beginning with such varied types of pickled skins as kidskins, skivers, lime-split cowhide and steerhide grains, good leather has been obtained in all cases, at least as good as with an equivalent amount of ZrO_2 as Zircotan N, and in some cases with a gain in plumpness and solidity. A tendency toward a smoother grain was also detected, since the reaction with acid does not liberate all the zirconium salt immediately, and since the rate of reaction can be controlled by varying the temperature and length of liquor. The higher content of available ZrO_2 in sodium zirconium silicate normally allows a reduction in amount used equal to one-third of the percentage of Zircotan N regularly used. In one instance it was possible to reduce the percentage by one-half, presumably because of the supplementary silica tannage. Some typical analyses of leathers from these tests are shown in Table VI.

TABLE VI

COMPOSITION OF ZIRCONIUM-TANNED LEATHERS

Kind of Leather	White Kid Suede		White Skivers	
Tanned with	Zircotan N	Sodium Zirconium Silicate	Zircotan N	Sodium Zirconium Silicate
% Given	10	7	20	10
% Ash	21.9	25.2	23.9	22.7
% ZrO_2	10.7	12.3	11.8	8.8
% SiO_2*	5.2	7.7	4.9	8.0
% Al_2O_3*	3.0	2.4	2.2	1.7

*Some of silica and all alum introduced with clay.

In recent years there has been a greater application of zirconium tannage on colored leathers, for example, in conjunction with chrome on suede-type leathers where the solidity which it confers results in a finer nap. Successful tannery experiments have been carried out using acidified sodium zirconium

silicate as a pretannage before chrome on colored kid and calf suede, and as a retannage on chrome side leather. In the latter case very little chrome was stripped, and after neutralizing, coloring, and fatliquoring an excellent piece of leather was secured. Typical analyses of leathers from these tests are shown in Table VII.

TABLE VII

COMPOSITION OF COMBINATION-TANNED LEATHERS

Procedure	Chrome Kid Suede Pretanned with Zr		Chrome Side Retanned with Zr	
Tanned with	Zircotan N	Sodium Zirconium Silicate	Zircotan N	Sodium Zirconium Silicate
% Given	8	5	5	3.5
% Ash	13.8	13.9	10.7	12.1
% ZrO_2	3.8	4.0	2.8	3.0
% SiO_2*	1.5	2.2	2.0	2.2
% Al_2O_3*	0.8	0.2	1.8	2.0
% CrO_3	5.5	5.3	2.2	2.2

*Some of silica and all alum introduced with clay.

We recognize that this approach to zirconium tannage is a radical one, and its regular application in tannery practice is, of necessity, still in an exploratory stage. With reasonably good supervision, however, no difficulties should arise in handling this reaction of acid with sodium zirconium silicate. The ultimate advantage lies in a much wider potential use of zirconium as a tanning material because of lower cost. Already a practical process of manufacture has been worked out, and a commercial product* is available at the same price as Zircotan N but with approximately 50% more ZrO_2. This means that the cost of this mineral tannage has been reduced by ⅓ to ½. If a sufficiently large market can be developed, the cost will be lowered even more. The immediate aim is to explore its further application in a cautious manner to ensure that leather of uniformly high quality will always be obtained.

SUMMARY

Exploratory tests opened up the possibility of utilizing some insoluble zirconium derivatives directly in tanning. Confirmatory tanning tests led to the selection of sodium zirconium silicate as the most promising material. Methods have been described for its successful application on a laboratory and tannery scale, leading to practical leathers tanned with zirconium at markedly lower cost.

* Zircotan S

We wish to take this opportunity of acknowledging the assistance of our colleagues in the extensive experiments described in this paper: for tanning tests, Mrs. Josephine Franecki, and Messrs R. F. M. Fisher, L. V. Hetzel, and E. A. Carlson; for analytical work, Mr. J. Wendkos and Miss Helen Franecke; for helpful advice, Dr. H. G. Turley.

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DISCUSSION

Dr. R. G. Henrich (B. D. Eisendrath Tanning Co.): This has been another fine paper in the zirconium series. It should arouse further interest in the use of zirconium as a tanning agent, especially since the use of the sodium zirconium silicate does reduce the cost considerably.

To start the discussion, I would like to ask Dr. Somerville one question. In case you do not want silica in the leather, or only a small amount of it, can the sodium zirconium silicate be applied in such a way that only a small amount of silica remains in the leather?

Dr. Somerville: It is a little difficult to do that working on pickled stock, because the silicic acid produced is in a very reactive form and is readily picked up by pickled stock. However, it is not fixed at such a low pH as the zirconium salt, and if necessary, ways could be worked out for partial neutralization and washing which would eliminate part of the silica.

Dr. William T. Roddy (Tanners' Council Laboratory): Dr. Somerville, when the zirconium is used as a retannage on the chrome whites, is there a possibility that this will improve the resistance of the chrome white to perspiration breakdown?

Dr. Somerville: Frankly, we have not done any experiments along that line, but I think that any material which combines with the fiber and increases the loading of the fiber will act in that direction. We have no quantitative measurements to that effect.

DR. WALLACE WINDUS (Tanimex Corporation): This is a very nice piece of work. How does your product compare with the products of Terres Rares and the tanning work of Progil? I am not familiar with the details of their work, but they have worked extensively with silicate ores of zirconium.

DR. SOMERVILLE: There are a number of products that have been described in the literature. There is "ZT23", which is 25-30% basic zirconium sulfate in admixture with SiO_2. They also have a product called "ZT45", and I believe there is one called "ZT45B", both showing higher basicity than ZT23. As far as we can tell, our approach gives more benefit from the silica as a tannage, or as a filler, than these products, because we form silicic acid right in the tanning solution, and it is more reactive in this state than an equivalent amount of dehydrated SiO_2.

MR. SELVARANGAN (Central Leather Research Institute, Madras, India): I would like to know the pH of the zirconium-tanned leather.

DR. SOMERVILLE: You must carry out the tanning in strongly acid solution, but you actually finish up with pH 3.5 to 5 in the leather.

MR. SELVARANGAN: Have you had any problem of gel formation?

DR. SOMERVILLE: We have not had any trouble with gel formation.

WASTED WORDS

Scientists who wish their research to become part of the "common pool of world scientific knowledge" must learn to write English or German, for publications in any other language stand an "overwhelming" chance of passing unnoticed. So concludes Knut Faegri, a Norwegian biologist, after an informal survey of international literature in botany.

Faegri checked the references at the end of technical papers in botanical journals from England, France, Germany, the Scandinavian countries, Switzerland, the U. S. and the U. S. S. R. English publications were overwhelmingly the most frequently cited. English and German publications accounted for more than 80 per cent of the citations in all except the French and Soviet journals. The French references were 56 per cent English and German; the Soviet references, 26 per cent.

American and British authors showed the narrowest linguistic spread; their references were, respectively, 84 and 78 per cent in the home tongue. Soviet scientists also lean heavily on their own language—73 per cent of their references were in Russian. But the Soviet lists were 27 per cent Western, while only two Western lists contained any Soviet references: the German (one-half per cent) and the Scandinavian (one per cent). The disparity, remarks Faegri, "is nothing new, but it is deplorable."

Faegri, who writes papers in two languages other than Norwegian (his report appeared in Britain's *Nature*), is "convinced that a brain that has the capacity for scientific work has also the capacity to learn so much of at least one foreign language as to be able adequately to express scientific ideas in it."

—*Scientific American*, April, 1956.

Discussion of an Adhesion Test for Leather Finishes

A paper entitled "Bonding Film Adhesion Test for Leather Finishes", by C. A. Burkart, N. D. Gallagher, and M. B. Neher, was published in the August issue of *JALCA*, pp. 418–29. The paper was originally presented at the Fifty-second Annual Meeting of ALCA, at Mackinac Island, Michigan, June 17–20, 1956, by Dr. Neher. The discussion following the presentation is given here.

DISCUSSION

Mr. Titus Weaver (Ohio Leather Company, Girard, Ohio): I should like to take this opportunity to express our appreciation to Dr. Neher for a very interesting paper. We in the Finish Committee have felt the need several times of a test of this type, especially one in which we can attribute some numerical values to the results that we get.

What evidence did you use in trying to determine whether any of the bonding film had penetrated the film in the finish?

Dr. Neher: That is a point which has been discussed many times and there is not any evidence other than the fact that there is a steep rise in the temperature adhesion curve at one point, and we must always try to stay below that point. In one leather that I had there was a steep rise and we stayed below that. In the others there is not much effect as you go up in temperature. We had to make the assumption at this point that, as long as you stay below the sharp rise, you are not getting any significant penetration of the finish by the bonding film.

Mr. Weaver: It would seem to me that in some cases you would get leather peeling with your film when you pulled them apart?

Dr. Neher: In the case of upholstery leathers particularly, this is true. If you have adhesion values in the range of ten pounds, that almost invariably is pulling leather off with the finish. In the lower results you do not normally get the finish pulling leather off.

Mr. Bernard Roll (Atlas Refinery, Inc., Newark, New Jersey): As Mr. Weaver said, the Finishes Committee is vitally interested in this question. I think Dr. Neher is to be congratulated on the information he has given us this morning. It seems to be original.

One point that is not obvious, I think, from your talk: When you pull the bonding surface away from the leather finish, do you always expect all of the finish to be removed from that spot of leather, or just part of it?

Dr. Neher: We would like to have it all removed. This is a function perhaps of oil in leather, or several other different factors. In many cases

there is complete removal of the finish, and this is what we would like to have. In other cases it is fairly complete. If removal is not complete, we do not consider it a satisfactory test. That has been one of the points involved—the search for new adhesives which will give complete removal of the finish.

MR. ROLL: All of this work is being done at elevated temperatures of 150°C. approximately?

DR, NEHER: That is right. We have tried to use adhesives that will set at room temperature, but we have not as yet found anything satisfactory that will work at room temperature.

MR. ROLL: If the test could be used at room temperature, it would more nearly correlate with what you expect the leather to do in performance, especially in shoe factory work?

DR. NEHER: That is right, and one of the things that needs to be done now is to get correlation of adhesion values with performance of the leather.

THE GENIUS OF THE "UNCOMMON MAN"

Behind every advance of the human race is a germ of creation growing in the mind of some lone individual whose dreams waken him in the night while others lie contentedly asleep. This was the contention of Crawford H. Greenewalt, president of Du Pont, in a speech before a recent meeting of the American Newspaper Publishers Association.

Greenewalt went on to say that the emphasis upon group effort in modern industry presents the serious problem of how to preserve the creative genius of the "uncommon man". It is a problem for management, for public education, for government, for the church, and for the press. And unless we can guarantee the encouragement and fruitfulness of the uncommon man, the future will lose for all men its virtue, its brightness and its promise.

—*Research and Engineering*, June, 1956.

PROPERTIES OF COLLAGEN FIBERS

A study of the mechanical properties of collagen fibers is being undertaken under a contract with the Eastern Regional Research Laboratory of the U. S. Department of Agriculture. Knowledge of the behavior of collagen fibers is meager, mainly because suitable methods of extracting the fiber from leather are not available. With its experience in the field of textile fibers, the Institute is in a good position to develop techniques for the purpose. The results of this investigation should provide valuable information on the relation between the mechanical properties of leather and its structure. The information will also add to the knowledge of the characteristics of protein fibers in general.

—*Textile Research Institute Membership News*, July, 1956.

Men cut large thongs of other men's leather. (*Ex alieno tergore lata secantur lora.*)

—A Latin proverb.

LIFE LINES

Brief Biographies of Our Contributors

ROBERT R. CALHOUN has been employed at the Eastern Utilization Research Branch of the United States Department of Agriculture since 1946 in designing and building instruments and apparatus for the research and engineering sections of the laboratory. He recently received the United States Department of Agriculture Superior Service Award in recognition of his outstanding work.

JOSEPH A. CASNOCHA was born in Binghamton, New York, where his father was associated with Endicott Johnson Corporation. He accompanied his family to Czechoslovakia where he enrolled in, and graduated from, the Bata Tanning Institute, at Batov. He returned to the United States in 1937, studied at New York University, and was connected with A. J. & J. O. Pilar, Inc., and with American Hide & Leather Co. He joined the Armed Forces in 1944 and was assigned to the Army Specialized Training Program at Yale University, where he remained until 1946. Since then he has been associated with the Leather Department, Dyestuff Division, of Sandoz Chemical Works, Inc. He joined ALCA in 1943.

MRS. JEANNE G. FEE received her B. S. degree with a major in Physics from Davis and Elkins College, Elkins, West Virginia, in June, 1952. After graduation she joined the staff of the National Bureau of Standards. Since 1954 she has been employed at the Eastern Utilization Research Branch of the United States Department of Agriculture in research on the physical properties of hide and leather.

C. H. GEISTER received his B. S. degree in Industrial Science and his M. S. in Chemical Engineering from Iowa State College. A fellow of the Mellon Institute of Industrial Research in Pittsburgh for 13 years and Technical Manager of Robert H. Foerderer, Inc., of Philadelphia for six years, he has been since 1936 Head of the Leather Division, Technical Laboratory, Organic Chemicals Department, E. I. du Pont de Nemours & Co., in Wilmington, Delaware. He has been a member of ALCA since 1930.

DR. J. S. KIRK has been associated with the leather industry for the past thirty years both in production and in research. He obtained his B. S. degree from Pennsylvania State University in 1924 and his Ph. D. from Cornell in 1931. He started his leather career at the firm of J. E. Rhoads and Sons, Wilmington, Delaware. In 1937 he joined the General Research Section of Du Pont where he conducted research in the tanning field. From 1945 to 1948 he was with the firm of Burk Brothers in Philadelphia as Chemist in control of production and development. In the latter year he accepted a position with General Dyestuff Corporation as Leather Department head.

When that corporation became a division of General Aniline & Film Corporation, he was transferred to Rensselaer to take charge of technical phases of the company's operations in leather. A member of ALCA since 1944, he has also served as chairman of the Convention Committee.

WILLIAM J. RAU, a graduate of Lehigh University, has been associated with the Rohm & Haas Company for twenty years. He has done research work on syntans and mineral tannage and has been co-author with Dr. Somerville of several papers on zirconium tannage.

IAN C. SOMERVILLE obtained his B. Sc. and Ph. D. degrees at the University of Edinburgh, Scotland. He has been with the Rohm & Haas Company for thirty years and is head of their Research and Development Laboratory on Leather Chemicals. His contributions to *JALCA* include papers on sulfiting of quebracho, on syntans, and on zirconium tannage. He joined ALCA in 1935 and received the Alsop Award in 1950.

DR. ROBERT STUBBINGS, a Research Assistant Professor in the Chemistry Department of Lehigh University, Bethlehem, Pennsylvania, received his Ph. D. degree from this department in 1949. He has been doing research in the field of leather technology since 1946, and in May of 1953 he became Director of the Division of Leather Technology at Lehigh. He has published many technical articles in the field of leather technology in the United States and abroad. Dr. Stubbings is a member of Sigma Xi, American Institute of Chemists, and the International Society of Leather Trades Chemists. He joined ALCA in 1946, is currently a member of the Council, and has been active on several technical committees.

DR. LEE P. WITNAUER received his B. S. degree from Canisius College, Buffalo, New York. In 1943 he joined the staff of the Eastern Utilization Research Branch of the United States Department of Agriculture as a Junior Chemist. He received his M. A. and Ph. D. degrees from Temple University Evening School with a major in Physical Chemistry. Dr. Witnauer holds the position of Unit Supervisor of the Physical Testing Unit of the Analytical, Physical Chemical and Physics Section and is an Assistant Adjunct Professor of Chemistry at Drexel Institute of Technology.

TO WASH LEATHER GLOVES

Place the gloves on the hands, and rub them with a soft sponge in lukewarm soap-suds. Wash off the soap-suds in clear water. Pull and stretch them, and put them in the sun, or before the fire, to prevent them from shrinking. When nearly dry, put them again on your hands, and keep them on till quite dry.

—*The National Encyclopaedia of Business and Social Forms.*
J. D. McCabe. Boston: E. W. Sawyer & Co., 1882.

ALCA NEWS

Proceedings, Reports, Notices and News

of the

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SECRETARY'S NOTICE

The A.L.C.A. - A.S.T.M. Joint Committee will meet Monday, October 22, 1956 at the Warwick Hotel, 65 West 54th Street, New York City. The meeting will last the entire day.

SECRETARY'S NOTE

The following committees have been appointed for 1957 by President Thorstensen:

AWARDS COMMITTEE

John Highberger, *Chairman*
H. B. Merrill
Walter Schultz

NOMINATING COMMITTEE

Arthur Kay, *Chairman*
Reuben Henrich
Dominic Meo

FRED O'FLAHERTY, *Secretary.*

INTERNATIONAL UNION OF LEATHER CHEMISTS SOCIETIES

ROME MEETING — 1957

PRELIMINARY ANNOUNCEMENT

The next biennial meeting of the International Union of Leather Chemists Societies will be held in Rome, Italy, from Sunday, September 15, to Thursday, September 19, 1957, under the auspices of the Italian Leather Chemists Society.

The International Commissions will meet during the morning and afternoon of Sunday, September 15. Delegates, members, guests, and visitors are expected to arrive during the day, and an official reception will be held that evening, probably in the City Hall.

The Conference will open officially on Monday morning, September 16, with addresses on behalf of the City of Rome and the Italian Leather Chemists Society, and lectures by noted authorities. It is planned to have an outstanding lecture on the subject of keratins, a Meunier memorial lecture, and a lecture on the leathers of ancient Rome.

On Tuesday, September 17, an all-day session is planned dealing with "The Manufacture of Leather". This is an innovation on the part of the international body, and it should provide great interest and a unique opportunity for an exchange of ideas of leather making on an international basis. This symposium should prove to be stimulating and perhaps provocative

because of the many leather-making practices in Germany, Britain, France, Italy, and other countries.

Wednesday, September 18, will be taken up with an all-day sight-seeing trip in Rome, with visits to museums and galleries. A luncheon will be held in Ostia, a famous resort on the seashore near Rome.

The presentation of scientific papers will continue on Thursday, September 19. In the evening an official banquet will close the Conference.

On Friday, September 20, tentative plans have been made for an audience with His Holiness, Pope Pius XII, at his summer residence in Castel Gandolfo.

Details of accommodations and reservations will be announced later.

It is suggested that those planning to attend make transportation arrangements shortly on account of the very heavy tourist traffic to Europe.

Members of ALCA are invited to submit papers which will be selected by the Executive Committee. Manuscripts should be forwarded to Mr. Harvey, Honorary Secretary, International Union of Leather Chemists Societies, 'Craigieburn", Duppas Hill Road, Croydon, Surrey, England.

REPORT OF THE HIDE EVALUATION COMMITTEE

W. R. Cox, *Chairman*

While there are many factors which affect the utility of hides and skins, such factors as skin damage, plumpness, skin diseases, and the like, appear to be beyond the scope of the committee at this time. At present, our efforts should be limited to a study of methods for assay of hide substance and an evaluation of the quality of cure as it has affected the leather-making potential of the stock. The Cincinnati Laboratory has undertaken what is perhaps the most complete modern investigation of the problem. Our committee has started with a consideration of the results of this work.

Cure Quality.—Much of the work on evaluation of cure quality has centered around either the volatile nitrogen or the water-soluble nitrogen present in cured hides. Although both of these values may well be useful indicators of hide cure, there is some question of their efficiency as neither is specific for hide substance *per se*. In order to obtain additional information on the point, comparison determinations of volatile nitrogen with water-soluble hydroxyproline (which is specific for hide substance) are being run by members of the committee and cooperating outside laboratories who have the equipment necessary to perform the rather difficult hydroxyproline determination.

Assay of Leather-Making Substance.—At Cincinnati, a lot of effort has been put into the development of a hide substance assay method. The work is divided into two phases: (1) the development of a sampling plan which will yield a representative result of adequate precision and (2) study of the analytical method involved. At present, their methods represent useful research tools but are not yet suitable for use as settlement basis between buyer and seller. A subcommittee has been appointed to study the sampling phase of the problem, and a series of round-robin analyses is contemplated to compare the moisture and ash determination.

The committee expresses the hope that the work at Cincinnati will be continued.

METHOD OF MAKING CLOTH AND LEATHER WATERPROOF

The minute spaces between the fibers of the yarn, either of cloth, silk, or cotton goods, cause them to be pervious to water; therefore, these minute channels in cloth and the pores of leather must be closed up in order to make them waterproof.

Many have been the means adopted and invented for the purpose, and some are quite simple enough to be adopted at home.

In waterproofing factories the process is carried on in rather a different manner to the house process. Rock alum, whiting, and water are the ingredients for producing a solution of alumine, in which the fabric is soaked; it is then passed through a solution of warm yellow soap water, to fix the alum in the interstices of the cloth, and enable it to resist the action of water, and so render the fabric waterproof. Then the cloth is washed and pressed. The proportions of ingredients for this process are as follows: 15 lbs. of materials; 1 1/2 lb. of rock alum; 1 1/2 lb. of common whiting; and 3 gallons of water. Soap solution temperature 100 Fahr.: 3 lbs. of yellow soap, 30 gallons of water, to 50 lbs. weight of cloth.

Another method is by immersion in a preparation composed of 2 oz. of pulverized alum dissolved in 1 pint of distilled water; and 1 oz. of dry white-lead rubbed down in one pint of water. The two solutions are mixed and allowed to settle; the liquor constitutes the required agent.

Another method by immersion: 1 oz. of dry white-lead rubbed down in half a pint of water; 1 oz. of pounded alum dissolved in half a pint of water; mix; and add 2 fluid drachms of acetic acid, and allow to settle.

When the cloth has been immersed in the liquor resulting from either of the above solutions, it is passed through a solution of quicklime, and a third time through a solution of Irish moss, which acts as a mucilage.

Waterproofing in the household may be easily managed thus: Boil half an ounce of Russian isinglass in a pint of soft water till dissolved; dissolve an ounce of alum in a quart of water; dissolve a quarter of an ounce of white soap in a pint of water; strain these solutions separately through linen and then mix them all together. Heat the liquid till it simmers and apply it with a brush to the wrong side of the cloth on a flat table. When dry, brush the cloth lightly with water. This process renders the cloth impervious to water, but not to air, and is therefore a healthy manner of rendering articles waterproof.

—*The National Encylcopaedia of Business and Social Forms*,
J. D. McCabe. Boston: E. W. Sawyer & Co., 1882.

ABSTRACTS

Committee for Physical Testing of Leather (S.L.T.C.). R. G. Mitton (Convener). *J. Soc. Leather Trades' Chemists*, **40,** 134–41, 150–62 (1956).—Text of revised methods. J.M.C.

Committee for the Chemical Analysis of Chrome-Tanned Leathers and Chrome Tanning Materials (S.L.T.C.). P. S. Briggs (Convener). *J. Soc. Leather Trades' Chemists*, **40,** 163–69 (1956).—Revised methods are given for determination of Cr in leathers, Cr tanning materials, and used Cr liquors; acid combined with Cr in Cr tanning materials; and pH of Cr Liquors. J.M.C.

Proposed Revised Official Methods (S.L.T.C.) for the Analysis of Oils, Fats, and Waxes. D. Burton and G. F. Robertshaw. *J. Soc. Leather Trades' Chemists*, **40,** 170–77 (1956).—Text of revised methods for sampling, separation of fatty matter from non-fatty matter, and determination of unsaponifiable matter, saponification value, acid value, and iodine value. J.M.C.

Fastness Tests Committee (S.L.T.C.). Proposed Official Method for the Assessment of Fastness to Washing of Leather. C. J. Pittard (Convener). *J. Soc. Leather Trades' Chemists*, **40,** 183–84 (1956).—The proposed method involves washing the specimen 5 times with soap for 30 min. at 40°C., with intervening rinsings. The change in color is determined by comparison with unwashed leather, using the standard gray scale. **Proposed Official Method for the Determination of Fastness to Daylight of Colored Leather.** *Ibid.*, 184–90. The method recommended is based on British Standard 1006:1955, which is also the recommended method of the International Organization for Standardization, and the Official Method of the Society of Dyers and Colorists. J.M.C.

Amino Acids, Fruit Acids, and Polyols of Myrobalans. D. E. Hathway. *Biochemical Journal*, **63,** 380 (1956).—A qualitative and exploratory study of the amino acids, plant acids, and polyols of myrobalans is reported. After removal of polyphenols and tannins from an 80% methanol extract, the remaining constituents were divided into neutral, basic, and acidic fractions by ion-exchange chromatography. Polyols were identified in the neutral fraction employing a paper chromatographic procedure. Glucose and sorbitol predominated in the mixture while approximately 1% of sucrose and of fructose was found. The amino acids determined by two-dimensional paper chromatography were typical of those detected in plant extracts in general. In addition to small quantities of phosphoric and succinic acids, a family of related cyclohexanecarboxylic acids was identified. J.M.C.

The Determination of 20–100 Micromilligram Quantities of Organic Nitrogen. D. Exley. *Biochemical Journal*, **63,** 496 (1956).—Details are given of an ultra-micro method to estimate organic nitrogen, consisting of a digestion with sulfuric acid containing selenium as a catalyst, and direct addition of Russel's (*J. Biol. Chem.*, **155,** 457 [1944]) reagents after neutralizing the digest. The method is said to be applicable to a range five times smaller than any previous method. The method is readily applicable to the micro scale (1.0–10.0 micrograms of nitrogen), with no special apparatus being needed. J.M.C.

Formation of Tannins by the Enzymatic Oxidation of Certain Phenolic Compounds. W. E. Elston, D. E. Hathaway, and K. G. A. Pankhurst. *Research Correspondence Suppl. to Research (London)*, **8,** No. 12, S64–65 (1955).—A collagen monolayer on water has a very low surface viscosity. If a tanning material is present in the solution, the viscosity of the monolayer rises very rapidly. Formation of tanning substances from various polyphenolic compounds, which in themselves have no tanning action, occurred when small amounts of H_2O_2 and horseradish peroxidase were added to solutions containing 2.3′.4′-trihydroxychalcone, gallic acid, catechin, 3′.4′-dihydroxyflavan, and protocatechuic acid. The time required for the viscosity of the collagen monolayer to attain a specified value increased, and hence the rate of formation of tannin decreased, in the order given for the above compounds. No tanning compounds were formed from resorcinol or hydroxyquinone. The probable mechanisms of the various oxidation reactions are discussed. H.B.M.

Color Measurement Committee (S.L.T.C.). Proposed Official Method for the Determination of Color Tolerances. J. S. Mudd (Convener). *J. Soc. Leather Trades' Chemists*, **40,** 191–94 (1956).—The chromaticity and luminance of the specimen, expressed in C.I.E. units, are determined by means of a Hilger photoelectric surface colorimeter, and compared with data for a standard. Differences between specimen and standard are expressed in multiples of T, representing a just noticeable difference under normal viewing conditions. J.M.C.

Investigations on Bating. I. A Historical and Critical Review of the Literature. G. H. Green. *J. Soc. Leather Trades' Chemists*, **40,** 195–204 (1956).—The literature on the mechanism of bating is reviewed historically. Although numerous theories have been proposed, none has been universally accepted as explaining all the known effects of bating on the pelt and on the final leather product. 38 references. J.M.C.

A Correlation of Tannin Content with Tannin-Formaldehyde Precipitate. F. R. Humphreys. *J. Soc. Leather Trades' Chemists*, **40,** 147–49 (1956).—A rapid method is given for the tannin analysis of *Pinus radiata* bark. The method involves precipitation of tannin with formaldehyde under controlled conditions and determination of the weight of the precipitate.

Analysis of the bark by official methods was used to obtain a correlation coefficient and a regression equation. A linear regression was shown to exist between the tannin content and the tannin-formaldehyde precipitate. J.M.C.

Processing Animal Hair in the Textile Industry. M. Clauss. *Das Leder*, **7**, 49–53 (1956).—The manufacture of felt is described. The secret of the felt-maker is in mixing various kinds of hair; up to 20 are used in a blend. All felt is now made by automatic machines. Felting is obtained by application of steam heat and movement. For dense felt the hair is carroted for several hours in 3° Bé H_2SO_4 to swell and spread the scales of the hair. Yarn is prepared much like felt, but the hair must be thoroughly washed. For yarn, hair must be at least 25 ml. long and must have an undamaged surface. To withstand wear and tear, carpet hair must be undamaged and must be carefully washed to remove any residues that might weaken it. Hair damaged by alkali will give trouble in carding. White or light-colored hair should be dyeable; this is not true of lime-pulled or sweated hair. For felt, the hair must be feltable. Hair removed by pasting or sweating is usually satisfactory, but calf or kid hair removed by one of these methods can be felted only after retreating. Limed hair is quite variable but usually satisfactory. I.D.C.

Notes on the Production of Combination-Tanned Leather. R. Bosse. *Das Leder*, **7**, 53–57 (1956).—Chrome retan leather now must meet more stringent requirements. Cheaper hides are being used, but smooth leather of good cutting value is required. The tannage must therefore give full flanks and smooth, tight grain but retain the chrome leather character. Increasing the amount of chrome offered or adding masking agents will increase fullness only to a limited extent. Pretanning with cationic chrome complex salts increases the reactivity of the hide to vegetable tannins, and this greater astringency can lead to disadvantages. The astringency problem may be solved by either (1) using special syntans or (2) filling the leather with nontanning dicyandiamide (Dicy) resins. If a suitable tailor-made syntan in neutral solution is added to chrome leather, the absorbed acid in the leather will lower the pH and cause detanning. Fixed mineral acid will hydrolyze and be replaced by tanning acid. There will be a slow, small increase in acidity, for there will be enough cations present to fix most of the liberated mineral acid. The tannage will therefore be mild and the leather full with a good grain. The second method of filling the leather is to use the method described by Dawson and Sellet (U. S. patents 2567238 and 2637622). Practical tanning suggestions for retan leather are given. The 2 filling methods are comparatively new, and how the conventional chrome tannage must be formulated is still a matter of discussion. The firmness of retan leather cannot be corrected by longer liming as this will cause loose grain, but skins for Dicy treatment may be opened up by 1 or 2 days in a white lime after the usual liming. A full chrome tannage is required to maintain the chrome character of the leather. Although the retanning deacidifies the leather, a moderate neutralization before retanning is desirable. If the leather is strongly retanned, it should be acidified somewhat; the pH of the retan liquor must not exceed 4.5 or, for Dicy, about 5.0. Retanning should be completed in 60–90 minutes. Resin filling is best accomplished by neutralizing the chrome leather to pH 4.4–4.6 with 1% (leather shaved weight)

of a mixture of equal parts of calcium formate and sodium sulfite, then adding the resin in 2 portions, with addition of boric acid between the resin treatments. The first portion of resin penetrates the leather, and the last is mainly retained in the surface layers. The retanned or resin-filled leather requires more fat liquor than normal. Before retanning, the leather is often preoiled with 0.5–0.7% of a medium-sulfonated sperm oil and 0.4% of castor oil. Oiling after tanning should be with a mixture of 2.5–3 parts of sulfonated oil to 1 part of nonsulfonated oil. Preoiling for resin-filled leather is difficult because the leather is more acid. After rinsing the resin-treated leather, it may be oiled with sulfonated sperm or neatsfoot oil, containing 3–5% SO_3 on the pure fat basis, to which 1/10 to 1/5 of the same unsulfonated oil has been added. Resin-filled leather loses water readily; therefore it must not be dried too sharply and must be stored after drying to permit it to regain a certain moisture content. I.D.C.

The Detection of Traces of Formaldehyde in Dried Hide and Skin Material. A. Küntzel and P. Falcoz. *Das Leder*, **7**, 107–9 (1956).—Some Persian dried goatskins that did not soak properly were tested for HCHO. In some of these skins HCHO could be detected, but in others, not. The question therefore arose as to whether HCHO could be present in amounts too small to be detected analytically, yet sufficient to harden the skin. The following quantitative test was tried: 6 g. of dry hide powder was treated for 2 hr. with 0.1% (on hide powder basis) of HCHO dissolved in 75 ml. of water. The pH was adjusted to 8.5 with NaOH. The mixture was then hydrolyzed for 80 min. with 10 ml. of *N* HCl in a pressure flask at 110°C. All the hide powder dissolved. HCHO was determined by the method of Brochet and Cambier in which it reacts with hydroxylamine hydrochloride liberating an equivalent amount of acid which is then titrated to pH 4.5 either with bromophenol blue or electrometrically. The results showed that there was a loss of about 20% of the HCHO. A series of dilutions of HCHO was tested qualitatively with the Gross-Bohle reagent—a SO_2-decolorized solution of parafuchsine (rosaniline) which reddens on addition of traces of aldehyde. The greatest dilution that gave a positive test was 1:200,000. The chromotropic acid test, in which a violet-rose color develops in the presence of HCHO in strong H_2SO_4, had a limit of 1:1,000,000, but when hide powder was treated with formaldehyde and hydrolyzed as above the limit was reduced to 1:800,000. Drops (0.05 ml.) of HCHO of different dilutions were placed on strips of dry, split collagen, dried, then soaked the following day. Hard spots that did not soak back well and appeared similar to those on the Persian skins were found at dilutions from 1:1 to 1:1000 but no hard spot was found at the spot treated with the 1:10,000 dilution. The hard spots were cut out, hydrolyzed (considerable dilution was necessary for hydrolysis) and tested by the chromotropic acid test. Spots from the 1:100 dilution gave positive, but those from the 1:1000 dilution negative, tests for HCHO. It is therefore possible for skins to have been treated with HCHO and yet to give no positive test for it. I.D.C.

Processing Pigskins. M. Hladnik. *Das Leder*, **7**, 57–60 (1956).—The principal breeds of hogs raised in Yugoslavia are listed. Excellent skins are obtained from stall-raised hogs. The first step in tanning should be to remove

fat by hand shaving and scraping; a machine for this purpose is not yet available. Soaking should be at 16°–18°C., preferably with a wetting agent. The skins may be limed with the usual sulfide lime, but if brush bristles are to be produced, a white lime should be used and the time of liming increased. Bating is the most critical operation in pigskin tanning. The skins should be bated for 3 or 4 hr. in a bate that is not too strong, and the temperature must not be above 32°–34°C. Chrome tannage can be by usual processes. If a vegetable tannage is used, changes in pH and concentration must be gradual, not abrupt. The amount of acid in the coloring or early liquors is important: too little acid will result in leather with a bad color, and too much acid will swell the skins too much. The strongest coloring liquor for pigskin should be about the same as the weakest for vegetable upper leather. The leather should have little uncombined tannin and therefore must be washed thoroughly. The fatliquor should be a neutral oil emulsified with an anionic emulsifier. Dyeing should be preceded by an acid or syntan bleach. No special finishing methods are required for either chrome or vegetable leather. I.D.C.

The Effect of Acetone Dehydration of Collagen on Its Swelling, Solubility, and Reactivity. K. H. Gustavson. *Svensk. Kem. Tidskr.*, **68,** 26–33 (1956) (In English).—It has been tacitly assumed that acetone-dehydrated, dried, and rehydrated collagen, much used in laboratory experiments, has the same properties as native collagen. This is true of bovine collagen, but not of codfish collagen. Codfish collagen, dehydrated with several changes of acetone, and dried at 30°C., was compared with native codfish collagen. The former showed less swelling, and less solubility in 0.1 *M* HCl, 0.02 *M* HCl + 2% NaCl, and 0.01 *M* CH_3COOH. No difference was observed in water or in 0.02 *M* HCl + 12% NaCl. Fixation of cationic Cr from 33% and 50% basic Cr chloride was the same for both collagens, but acetone-dehydrated codfish collagen fixed less Cr from 67% basic Cr chloride and from Cr sulfite and oxalate liquors, rich in non-ionic Cr complexes. Fixation of wattle tannin was the same for both native and acetone-dehydrated collagen. These experiments were repeated with acetone-dehydrated, dried, and rehydrated calfskin collagen, and no differences from native calf collagen were found. Codfish collagen, acetone-dehydrated and then rehydrated without drying behaved like native cod collagen, showing that the lowered swelling capacity, solubility, and reactivity towards non-ionic Cr are caused by drying rather than by any specific effect of acetone. It is suggested that OH groups of codfish collagen form new links with groups other than peptide groups on drying. Some support for this hypothesis is given by a small (2°C.) increase in shrinkage temperature for the dehydrated cod collagen. Data are given for solubility of native cod collagen in HCl solution containing 2% salt, at pH values from 5.1 to 1.5, in 24 hr., at 20°C. (1.2 g. collagen in 100 ml.). Maximum dissolution (85%) occurred at pH 2.5. Under the same conditions only 1.2% of bovine collagen is dissolved. H.B.M.

Volumetric Determination of Zirconium. An Ethylenediamine Tetraacetate Method Involving Back-titration with Bismuth. J. A. Fritz and M. Johnson. *Anal Chem.*, **27,** 1653–55 (1955).—The Zr solution is brought to pH 2 and treated with a measured excess of standard ethylenediamine tetra-

acetic acid (EDTA) solution, and the excess EDTA is back-titrated with standard $Bi(NO_3)_3$ solution in the presence of thiourea, which gives a yellow color with Bi^{+++} at the end point. If sulfate or phosphate is present, ammonum tartrate is added and the solution is boiled before the back-titration. Aluminum, if present, forms a complex with EDTA which decomposes very slowly during the back-titration. This can be overcome by adding a Cu^{++} salt before the EDTA, to form the more easily decomposed Cu—EDTA complex. Fe^{+++} is determined along with Zr, and must be corrected for by a separate determination. Interference by Ti can be overcome (if not more than 5 mg. of Ti is present) by adding a large excess of $(NH_4)_2SO_4$. Fluoride, if present, must be expelled by evaporating with $HClO_4$ or H_2SO_4 before making the determination. For details, the original publication should be consulted. H.B.M.

An Improved Volumetric Method for Zirconium. G. W. C. Milner and J. W. Edwards. *Analyst* **80,** 579–84 (1955); *Chem. Abstr.*, **50,** 710*e* (1956).

The Decomposition of Collagen and Procollagen with Sodium Periodate and Phenyl Isocyanate. W. Grassmann and K. Kuhn. *Hoppe Seyler's Z. Physiol. Chem.*, **301,** 1–6 (1955) (English summary); *Chem. Abstr.*, **49,** 16005*c* (1955).

Amino Acid Composition of Collagen and Gelatin of Man, Ox, Pig, Whale and Wallaby. J. E. Eastoe. *Biochem. J.*, **61,** 589–600 (1955). **Appendix. Notes on the Determination of Amino Acids by Ion Exchange Chromatography.** *Ibid.*, 601–3; *Chem. Abstr.*, **50,** 3582*h* (1956).

The Effect of Breed, Sex, Weight, and Hide Location on the Properties of Pig Velour Leather. F. Stather, H. Herfeld, and W. Hartung. *Ges. Abhandl. Deut. Lederinsts. Freiberg/Sa.*, **10,** 16–33 (1954).—A 3-factor experiment was carried out on skins from white and black breeds, light and heavy carcasses, and male and female pigs. Tests were made on specimens from butt, neck, and belly. These tests included histological examination, fat content at various process stages, number of bristle holes per $cm.^2$, area and weight yields, appearance of the finished leather, chemical analyses, and physical tests. Histological examination showed that the corium of pigskins is almost free from fat cells. The high fat content of pigskins arises from 2 causes: first, the sub-cutaneous tissue, composed almost entirely of fat cells, intrudes into the corium around the bases of the bristles, and some of this tissue is left on the skin after fleshing; second, migration of fat from sub-cutaneous tissue into the corium occurs on storage. The number of bristle holes per $cm.^2$ decreases from the butt towards the neck and belly, and is lower for heavy skins, female skins, and black skins compared to light, male, and white skins respectively. Chemical and physical tests showed no pronounced differences. Heavy pigskins are not suitable for velour. Surprisingly, the wettability, water absorption, and air permeability were decreased rather than increased by buffing. H.B.M.

Tanning Investigations for the Reduction of Consumption of Babul Bark in North Indian Bag Tanning by Using Mixtures of Sodium Sulfite and Bisulfite in the Tannage. O. S. Davood and B. M. Das. *Bull. Central Leather Research Inst., Madras*, **2**, 291–300 (1956).—In "bag tanning", the surface-tanned sides are sewn into the form of bags, which are filled with babul bark: liquor is poured onto the bark, percolates through the skin, and is returned repeatedly until the skin is tanned. This cottage industry produces a very cheap sole leather, and operates on a slender margin of profit. Tests showed that the addition of 0.5% each of Na_2SO_3 and $NaHSO_3$ to the bark made possible a 5–10% reduction in the amount of bark used. The yield was not impaired, and the color of the leather was improved. Larger additions (2%) are neither economically beneficial nor necessary. H.B.M.

Spectrophotometric Studies in Leather Research. III. Determination of the Phenolic Hydroxyl and Tannin Contents of Vegetable Tanning Materials by the Differential Ultraviolet Spectrophotometric Method. *Bull. Central Leather Research Inst., Madras*, **2**, 285–90 (1956).—Compounds containing phenolic OH groups show 2 absorption maxima, at 290–320 mμ. and 235–250 mμ. These absorptions cannot be used for estimation of phenolic OH content, because of pH effects and interfering substances, but Goldschmid (*Anal. Chem.*, **26**, 1421 [1954]) and Maranville and Goldschmid (*ibid.*, p. 1423) showed that the phenolic content could be obtained from the difference between the maximum absorptions in alkaline and in acid solutions. The authors applied this differential absorption technique to 11 tanning extracts. In all cases the differential absorptions, both at 290–320 mμ. and at 235–250 mμ., were linear functions of solids content. However, a different factor, based on the hide powder determination, would be required for each extract in order to obtain the tannin content from the differential absorption. The authors attempted to determine total OH groups (from differential absorption at 235–250 mμ.) and non-conjugated OH groups (from differential absorption at 290–320 mμ.), by comparison with the differential absorptions of a number of polyphenolic model substances of known structure. No correlation existed between the phenolic contents thus determined and the tannin content by the hide powder method. However, the tanning materials studied fell into 3 well marked groups, according to decreasing percentages of non-conjugated OH groups and ratio of non-conjugated to total OH groups, as follows: (1) quebracho, *Terminalia arjuna*, dhawa; (2) wattle, karada, *Cassia marginata*, *Hopea parviflora*, cutch; (3) myrobalans, chestnut, divi divi. This line of attack may ultimately be useful in elucidating the structures of tanning compounds. H.B.M.

Use of Ammonium Lignosulfonate in Tanning Processes. S. R. Annett. *Can. Chem. Processing*, **39**, No. 4, 97–98 (1955); *Chem. Abstr.*, **49**, 16486c (1955).

Chromatographic Studies on Spruce Bark Extract. G. Lindstedt and B. Zacharias. *Acta Chem. Scand.*, **9**, 781–92 (1955); *Chem. Abstr.*, **49**, 16486a (1955).

Influence of Temperature in Vegetable Tanning. P. J. Van Vlimmeren. *Ned. Leder-Ind.*, **62,** 100–2, 131–34, 180–83, 234–35 (1951); *Chem. Abstr.*, **49,** 11309*h* (1955).

Tannin Decomposing Enzymes of Molds. II. H. Nishira and N. Mugibayashi. *Science Repts. Hyogo Univ. Agr., Ser. Agr. Chem.*, **2,** 1–4 (1955). **III. A Simple Method for the Determination of Enzyme Activity.** N. Mugibayashi, H. Nishira, and I. Kubo. *Ibid.*, 5–7; *Chem. Abstr.*, **50,** 10153*c* (1956).

Analysis of the Acid—Base Behavior of Gelatin. J. Salvinien and S. Combet. *Compt. Rend.*, **242,** 114–16 (1956); *Chem. Abstr.*, **50,** 10159*f* (1956).

The Role of Nonalbumin Constituents in the Formation of the Procollagen Structure. A. L. Zaides, A. A. Tustanovskii, and G. V. Orlovskaya. *Doklady Akad. Nauk. S.S.S.R.*, **104,** 553–56 (1955); *Chem. Abstr.*, **50,** 9826*b* (1956).

Method for the Estimation of the Unoxidized Sugar and Formic Acid in Chrome Liquors. T. J. Devassy. *Bull. Central Leather Research Inst., Madras*, **2,** 281–84 (1956).—Sugars are determined by oxidation with alkaline K_3 Fe $(CN)_6$ using methylene blue as indicator (Coles's method). The liquor is freed from Cr by precipitation in the cold with NaOH at pH 5–6, and filtration after standing overnight. The filtrate is brought to pH 1.1 (same pH as standard hydrolyzed sucrose solutions used as standards) and made to 250 ml. This solution is added from a buret to a known amount of $K_3Fe(CN)_6$, which depends upon the expected concentration of sugar in the dechromed solution. For concentrations of 5.0–0.2, 1.0–0.1, and 0.1–0.01% sugar, the quantities are 10, 5, and 1 ml. of 1% $K_3Fe(CN)_6$ solution respectively. This is mixed with 10 ml. of 2.5 *N* NaOH and 10 ml. H_2O, heated to boiling, and titrated with the sugar solution until the yellow color fades; then 1 drop of 0.1% methylene blue solution is added, and the titration is continued till the blue color is discharged. Sugar content is obtained by reference to curves obtained by titrating the same amount of $K_3Fe(CN)_6$ with standard sugar solutions of various strengths, prepared by hydrolyzing known weights of sucrose with HCl. The method was tested by adding known weights of sugar to $Cr_2(SO)_4$ solutions; recoveries were 99.2–100%. Addition of oxalic, tartaric and formic acids did not interfere. Formic acid was determined by oxidation with bromine in the presence of pyridine and back-titration with $Na_2S_2O_3$ (Longstaff and Singer, *Analyst*, **78,** 491 [1953].). The HCOOH is steam-distilled from the acidified Cr liquor and collected in dilute NaOH. The distillate (about 700 ml.) is concentrated to about 20 ml., transferred to an iodine flask surrounded with ice water, acidified, and treated with 2.5 ml. of purified pyridine and 20 ml. 0.1 *N* Br in glacial CH_3COOH. After 3 min., the excess Br is back-titrated with $Na_2S_2O_3$. A blank is run using water in place of the HCOOH solution. The method was tested on $Cr_2(SO_4)_3$ solutions after adding known amounts of HCOOH and aging overnight. Recoveries were 99.2–99.9%. H.B.M.

Effects of Tannery Waste Waters on Organisms of Surface Waters. S. Wlodek. *Roczniki Panstwowego Zakladu Hig*, **6,** 303–22 (1955) (English summary); see *Chem. Abstr.*, **50,** 9774*e*.

Benzoate Method for Determining Aluminum. A. Ya. Sheskol'skaya. *Zhur. Anal Khim.*, **11,** 102–5 (1956); see *Chem. Abstr.*, **50,** 9211*b*.

The Interrelationship Among the Fibrous Structures of the Connective Tissue in the Light of the New Data Concerning the Structure of Collagen. G. V. Orlovskaya. *Arkh. Patol.*, **18,** No. 1, 68–74 (1956); see *Chem. Abstr.*, **50,** 8762*b*.

The Combination of Collagen A and Chondroitinsulfuric Acid. S. Bazin and A. Delaunay. *Compt. rend.*, **242,** 834–36 (1956); see *Chem. Abstr.*, **50,** 8773*b*.

Collagen. VIII. Action of Chondroitinsulfuric Acid on Solutions of Collagen A. A. Delaunay and S. Bazin. *Bull. assoc. diplômés microbiol. fac. pharm. Nancy*, **No. 62,** 5–16 (1956); see *Chem. Abstr.*, **50,** 8773*f*.

Tanning Properties of Chrome Liquors Prepared with Organic Reducing Agents. I. Reduction Efficiency of Some Organic Substances. Y. Sakimoto and T. Osugi. *Mem. Fac. Agr. Hokkaido Univ.*, **3,** 361–66 (1953); see *Chem. Abstr.*, **50,** 8237*h*.

Tanning Raw Hides Without Wool with Chrome Tan Liquors Made from Sodium Monochromate. S. A. Kuraites. *Legkaya Prom.*, **15,** No. 10, 30–41 (1955); see *Chem. Abstr.*, **50,** 8239*a*.

The Estimation of Sulfhydryl Groups in Wool by Means of 1—(4-Chloromercuriphenylazo)—Naphthol—2. R. W. Burley. *Textile Research J.*, **26,** 332–40 (1956).—The degreased fibers are treated with the reagent dissolved in formamide. Part of the reagent combines with –SH groups. The uncombined reagent is determined colorimetrically, and the amount of reagent combined, and hence the –SH content, is determined by difference. For intact fibers a contact period of 14 days is required. This is reduced to about 2 days by super-contracting the fibers by boiling in aqueous phenol for not more than 10 minutes, or by grinding them to a powder under water before making the test. Longer heating in phenol gives lower results, and grinding in air gives higher results for –SH groups. The reagent must contain about 1% water and show a pH value of about 8 after dilution with 5 parts of water. At pH 9, results are high, and no equilibrium is reached, presumably due to action of alkali on –S–S– groups. Merino wools contain about 20 micromols –SH per g., and Cape mohair about 30. The reliability of the method was demonstrated by tests on other sulfhydryl-containing compounds, and on wools in which the number of –SH groups had been increased or decreased by reducing agents and blocking agents respectively. H.B.M.

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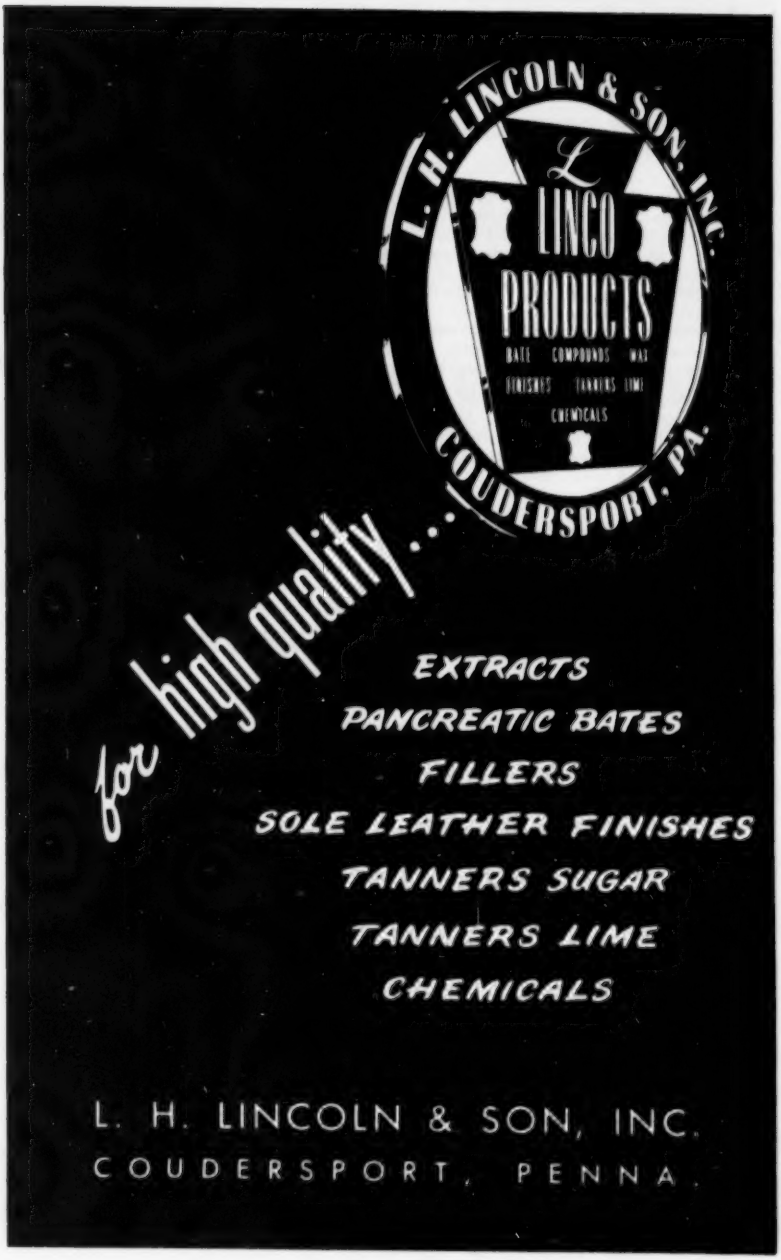
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THE TANNERS' COUNCIL RESEARCH LABORATORY

at

THE UNIVERSITY OF CINCINNATI

is

THE DEPARTMENT OF BASIC SCIENCE

in

THE GRADUATE SCHOOL OF ARTS AND SCIENCE

The purpose of the laboratory is to conduct scientific research in the fields of Science concerned with Tanning and Leather.

To train Chemists in the technique of research and prepare them for Industry.

This Laboratory serves as the Official Technical Headquarters for the Tanning Industry of the United States.

Your inquiries will be gladly answered.

Address DR. FRED O'FLAHERTY, Director
Tanners' Council Laboratory
University of Cincinnati
Cincinnati 21, Ohio.

Technology is the
handmaiden of
all chemical Industries
Technology is
born of Research

Fred O'Flaherty

RESEARCH

has Two functions

To produce a better Product and
to do it More Economically.

**THE TANNERS' COUNCIL
RESEARCH LABORATORY**

UNIVERSITY OF CINCINNATI

**THE TANNERS' COUNCIL
RESEARCH LABORATORY**

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We serve the Tanning and Leather Industry
through a broad program of Research.

Solvent Tannage,
born of Science is
a chemical Process
Industry — Be Prepared

Fred O'Flaherty

INDEX TO ADVERTISERS

ACADEMIC PRESS INC. XXX
ADOLF SCHUBERT XXXV
AMERICAN CYANAMID COMPANY, Dyestuff Department XVII
AMERICAN EXTRACT CO. ..... Outside Back Cover
APEX CHEMICAL CO., INC. XXXII
ARKANSAS COMPANY, INC. VII
ARTHUR C. TRASK CO. XXXI
ARTHUR THOMAS CO. XX
ATLAS REFINERY XVI
BARIUM REDUCTION CORPORATION XXIII
BARKEY IMPORTING CO., INC. XIV
BONA ALLEN, INC. XXXIV
BUCKMAN LABORATORIES, INC. XII
CHEMTAN COMPANY XIX
CLINTON CORN PROCESSING COMPANY XXXIV
EISENDRATH TANNING CO. XXV
FRANK CRYSTAL III
FRANK F. MARSHALL XXXI
GARDEN STATE TANNING INC. XXXI
GEIGY COMPANY, INC. IX
HOOKER ELECTROCHEMICAL CO. XI
HOWES LEATHER CO., INC. XXXIV
INTERNATIONAL PRODUCTS CORP. X
KEPEC CHEMICAL CORPORATION XXXI
LEATHER AND SHOES V
LEATHER MANUFACTURER, THE XXVII
L. H. LINCOLN & SON, INC. XXIX
MARDEN WILD CORPORATION XXIV
MUTUAL CHEMICAL DIVISION, ALLIED CHEMICAL & DYE CORP. ..... Inside Back Cover
NEWARK LEATHER FINISH CO. XXXIII
NOPCO CHEMICAL CO. XXI
OHIO LEATHER CO., THE XXV
OLSON IMPORTING COMPANY, INC., THE ..... Inside Front Cover
PRESTO COLOR CO. XXVI
REILLY-WHITEMAN-WALTON CO. XXVII
RIVER PLATE CORPORATION, THE IV
ROBESON PROCESS CO. II
ROHM & HAAS I
SALEM OIL & GREASE CO. XXVIII
SAXE CUTCH CORPORATION XXIV
SHOE & LEATHER REPORTER XXVIII
SOCONY MOBIL OIL CO., INC. ..... Insert
SOLVAY PROCESS DIVISION, ALLIED CHEMICAL & DYE CORP. VI
SOUTH AFRICAN WATTLE EXTRACT MFRS. ASSO. XV
SUN OIL COMPANY XXIV
TANEXCO, INC. XXXVIII
TANIMEX CORPORATION XIII
TANNER'S COUNCIL RESEARCH LABORATORY ..... XXXI—XXXV—XXXVI
UNION STARCH & REFINING CO. XXXII
UNITED STATES BORAX & CHEMICAL CORP. XXVI
UNITED STATES TESTING COMPANY XXXIII
WALLERSTEIN COMPANY, INC. XXII
WARNER CO. XXV
WHITTEMORE-WRIGHT CO. XXVI
WOLF, JACQUES & CO. VIII
YOUNG CO., J. S. XVIII

MYRTAN

A TANNING EXTRACT

made from the wood of an Australian species of the Eucalyptus family. It contains both catechol and pyrogallol tannin, the latter predominating.

TYPICAL A.L.C.A. ANALYSIS

	Ordinary	Clarified
TANNIN	61.55	64.34
NON-TANNIN	16.03	17.14
INSOLUBLES	1.70	0.72
WATER	20.72	17.80

As a retanning agent for chrome tanned leather, Myrtan possesses many advantages, such as smooth and strong grain, good color and break, as well as a round feel.

Blended into sole leather tonnages, it has given better yields and improved color.

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Cr_2O_3	24%	25%
Basicity (Schorlemmer)	33%	52%

Koreon is packed in multi-wall paper bags containing 75 pounds, and in fibre drums containing about 325 pounds.

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